A SPECTROSCOPIC STUDY OF SOME PLATINUM SILYL AND RELATED COMPOUNDS

by

Duncan Wardlaw Wilson Anderson

A Thesis presented for the degree of Doctor of Philosophy

University of Edinburgh

July, 1973

Acknowledgements

I am most grateful to those who have helped in carrying out the work described here. In particular, I would like to thank my supervisor, Professor E.A.V. Ebsworth, for his continual help and encouragement over the three years.

I would also like to thank Dr. D.W.H. Rankin for his help and guidance in all the electron diffraction and n.m.r. double resonance experiments and Dr. J.E. Bentham for initiating me into the techniques of vacuum-line chemistry.

I am grateful to the Salters' Company for a maintenance grant, the University of Edinburgh for provision of laboratory facilities and Professor D.W.J. Cruickshank and Dr. B. Beagley (Manchester University) for the provision of facilities for electron diffraction.

I am also grateful to Mrs. Carter for patiently typing the thesis and Mr. Baxter for photographing the spectra.

Summary

This thesis describes some spectroscopic studies of a series of bis-(triethylphosphine) complexes of platinum.

Using heteronuclear double resonance techniques, the platinum and phosphorus n.m.r. spectra of these complexes have been considered. The variations in $\delta(^{195}Pt)$ and $\delta(^{31}P)$ with change of ligands bound to platinum have been studied and the general trends are discussed. The use of this technique, in particular the values obtained for $\delta(^{195}Pt)$, as a means of identification of reaction products is demonstrated.

The preparation and characterisation of a series of six-coordinated platinum hydride complexes, of general formulae cis-trans-$[PtH_2XY(PEt_3)_2]$ and cis or trans-trans-$[PtHXY_2(PEt_3)_2]$ (X, Y = halogen) is described. They are formed by oxidative addition of HX to trans-$[PtHY(PEt_3)_2]$ and trans-$[PtY_2(PEt_3)_2]$ respectively in solution at reduced temperatures; mechanisms have been proposed for these reactions. The products were identified by their n.m.r. parameters, in particular by $\delta(^{195}Pt)$ and $\tau(PtH)$. In addition, for $PtH_2X_2(PEt_3)_2$ (X = Cl, Br) vibrational spectra and C,H analyses have been recorded. Attempts to use cis-cis-trans-$[PtH_2I_2(PEt_3)_2]$ as a hydrogenating agent are considered.

Some silyl and germyl platinum complexes, trans-$[Pt(MH_2X)Y(PEt_3)_2]$ (M = Si, Ge; X = CCH, $CCCF_3$, CN, C_5H_5;

Y = halogen) have been prepared by the reaction of silyl and germyl compounds, MH_3X, with platinum hydrides, trans-$[PtHY(PEt_3)_2]$. The n.m.r. parameters of these compounds are discussed and a mechanism for the preparative reaction of oxidative addition of M-H followed by elimination of H_2 is postulated. No interaction between the group Y and platinum was observed. The reactions of silyl halides with trans-$[Pt(CCX)_2(PEt_3)_2]$ (X = H, Ph, CF_3) and trans-$[Pt(CH_3)\ I\ (PEt_3)_2]$ have been used to test the postulate that the rate determining step in the addition-elimination mechanism is the electrophilic attack of SiH on Pt. This was confirmed; the acetylenic group deactivated the platinum while the methyl group activated it towards oxidative addition.

Silyl and germyl complexes of palladium, trans-$[Pd(MH_{(3-n)}X_n)Y(PEt_3)_2]$, (M = Si, Ge; X, Y = halogen, n = O to 2) have been prepared by the action of MH_3X on trans-$[PdY_2(PEt_3)_2]$. They have been characterised by comparison of their n.m.r. parameters with the platinum analogues; further characterisation was not possible because of the instability of the products. An addition-elimination mechanism has been proposed for the formation of these compounds.

MH_3CCCF_3 (M = Si, Ge) have been prepared and characterised and the molecular structures of SiH_3CCH, SiH_3CCCF_3, CH_3N_3 and CH_3NCS have been determined by gas phase electron diffraction.

Contents

CHAPTER 1

MAGNETIC DOUBLE RESONANCE STUDIES OF SOME TRANS-BIS(TRIETHYLPHOSPHINE) COMPLEXES OF PLATINUM

1.1. Definitions and Sign Conventions

Ξ (X) is defined as the resonant frequency of X in a polarising magnetic field of strength such that tetramethylsilane gives a resonance at exactly 100 Mc/sec. Corrections have to be applied to the observed resonant frequency to bring the tetramethylsilane resonance to 100 MHz. These corrections take into account the lock signal used, if other than tetramethylsilane, any instrument offset due to the mode of operation and offsets due to small variations from 100 MHz in the frequency produced by the instrument.

The chemical shift [δ(X) in p.p.m.] of a nucleus X can be quoted either to high field or to high frequency of the standard chosen. Since most modern instruments operate at a fixed field strength and vary the frequency applied, the convention chosen for the following work is the latter. The chemical shift of a nucleus is defined as positive if the resonant frequency of that nucleus in a polarising magnetic field is higher than the frequency of the nucleus in the standard compound. The standards used in the following work are,

For ^{195}Pt, 0.5 M solution of trans-$[PtClH(PEt_3)_2]$ in CH_2Cl_2 at 293K.

For ^{31}P, 85% H_3PO_4

For ^{29}Si, $Si(CH_3)_4$

For ^{19}F, CCl_3F

The coupling constant ($^{n}J(MQ)$ in Hz) between two coupled nucleii M and Q separated by n bonds is defined as positive when the state with the two nuclear spins antiparallel is the one of lower energy[1]. In general the sign is not measured directly but is determined by relating it, using heteronuclear double resonance techniques, to a coupling constant of known sign in the molecule. Ultimately the signs of all coupling constants are referred back to $^{1}J(^{13}C - ^{1}H)$ which is defined as positive.

1.2. Introduction

In 1946 Bloch[2] discovered that, if a sample of water was placed in a variable magnetic field and subjected to a radiofrequency, a resonance signal was obtained. This was the birth of nuclear magnetic resonance spectroscopy and since then it has become a widely used tool, not only in chemistry, but in many branches of science. ^{1}H is probably the most widely studied nucleus because of its natural abundance (99.98 %, $I = \frac{1}{2}$), its large magnetic moment (μ = 2.79270 B.M.) and its presence in most commonly studied compounds. A considerable amount of the work involved in the following chapters depends on ^{1}H n.m.r. as a means of identifying products. However other nuclei have isotopes with a nuclear spin quantum number of $\frac{1}{2}$; their natural abundances, magnetogyric ratios and relaxation times vary widely. In recent years much work has been done on studying the resonances of these

other nuclei. In many cases these atoms are directly involved in changes through a reaction whereas the protons may be several atoms removed from the active sites; therefore this results in this type of n.m.r. spectroscopy being considerably more sensitive to the changes. This is particularly true of the transition metals where changes in the co-ordination sphere are being considered. In comparison with the ^{1}H shifts of protons on the ligands, a much wider range in chemical shifts of the central atom is observed. Even relatively small structural changes, like different isomeric forms, can readily be detected.

Two techniques have been used to study the resonances of these heavy nuclei. One method is by direct observation. If the magnetic field and radiofrequencies are adjusted to bring the nucleus into resonance, then the spectrum can be observed in the normal manner. In this way magnetogyric ratios and chemical shifts for compounds of $^{55}Mn(I = 5/2)$ [3,4], $^{59}Co(I = 7/2)$ [5,6], ^{195}Pt [7,8] and ^{199}Hg [9] have been determined. However since most heavy nuclei with $I > 0$ have small natural abundances, magnetogyric ratios and relaxation times, direct observation of their resonances is often difficult.

The second technique used is that of heteronuclear double resonance. The spectrum of one nucleus n_1 (normally ^{1}H), which couples with the heavy nucleus n_2, is observed and a second radio-

frequency is applied to the sample. When the second RF reaches the resonant frequency of n_2, a 'decoupled' spectrum is obtained. By reducing the RF power and varying its frequency associated with n_2 a 'plot' of the spectrum of n_2 can be obtained. This technique has the advantage that it utilises the sensitivity and relaxation time of ^{1}H.

1.2.(a) Chemical Shifts of Heavy Nuclei

Heteronuclear double resonance determinations of the chemical shifts of heavy nuclei have a wide range of applications. They have been used to gain information about the effect of ligands on the environments of the nuclei, to correlate with other spectroscopic properties and theoretical calculations and as a means of identification of reaction products.

Ξ (^{199}Hg) in a series of aryl and pentafluoroaryl mercury compounds has been determined [10]. A shift of 9060 $\pm$ 60 Hz to high field is observed in the change from $(C_6F_5)_2Hg$ to $(C_6F_5)Hg\,OAc$. This has been attributed to the effect, on the paramagnetic shielding term, of changing the electronegativity of the ligands. The relative signs of $J(^{199}Hg - ^{19}F)$ and $J(^{199}Hg - ^{1}H)$ were also determined.

Most work in this field has been done on complexes of platinum. This is probably due to the large number of stable complexes available and the high natural abundance of ^{195}Pt

(33.7%). In a series of square planar complexes of platinum (II) containing phosphorus or chalcogen ligands [$(RO)_3P$, R_3P, R_2S, R_2Se], a range in $\delta(^{195}Pt)$ of over 1600 p.p.m. was observed [11]. It was suggested that this was a result of the paramagnetic shielding contribution being dominant in determining the chemical shifts.

Confirming this a correlation between $\delta(^{195}Pt)$ and ΔE (the crystal field splitting), as measured roughly by the colour of the complex, was found. No correlation between $\delta(^{195}Pt)$ and the trans effect of the ligands was found.

A similar type of correlation has been detected for complexes of the type trans-$[PtHL(PEt_3)_2]$ where L is an anionic ligand [12].

Changes in $\delta(^{195}Pt)$ were interpreted in terms of variations in the paramagnetic shielding term which arose from changes in the σ and π covalency of the Pt-L bond. The order of ^{195}Pt chemical shifts for the platinum hydrides varied with L in the order

$$RCO_2^- < NO_3 < NO_2 < Cl < -SCN < Br < CN < I$$

which differs markedly from the spectrochemical series for these ligands. It was therefore deduced that, for these compounds, changes in ΔE were not the dominant factor in determining $\delta(^{195}Pt)$.

Pidcock [7] applied Ramsey's Equation [13] to some square-planar complexes of platinum (II) and obtained an equation in which the paramagnetic shift was proportional to a linear combination of wavelengths of two transitions in the absorption spectrum.

However, using ^{195}Pt chemical shifts obtained by direct observation, they found virtually no correlation between $\delta(^{195}Pt)$ and the parameters from the electronic absorption spectra.

A good example of the power of the double resonance technique is given in the determination of ^{103}Rh chemical shifts in a mixture of cis- and trans-$[Rh(MeSCH_2.CH_2SMe)_2Cl_2]Cl$ [14]. There were seven isomers present in D_2O at 295K but the total spread of $\tau(CH_3)$ was 0.34 p.p.m. Chemical shifts of ^{103}Rh showed a spread of 296 p.p.m. with a range of 83 p.p.m. for the four possible orientations of the methyl groups in the trans isomer.

1.2.(b) Coupling Constants in Transition Metal Complexes

Heteronuclear double resonance techniques can also be used to determine the magnitudes of coupling constants; these values have been used quite extensively in investigating the nature of metal-ligand bonds. Signs of coupling constants, in simple systems, can only be found by double irradiation. The coupling constants in the complexes cis- and trans- $[PtCl_2(PEt_3)_2]$ [15] and trans-$[PtClH(PEt_3)_2]$ [16] have been determined in this way. By ^1H-^{195}Pt double resonance, it was deduced that both $^1J(^{195}Pt - ^{31}P)$ and $^1J(^{195}Pt - ^1H)$ were positive.*

---

* They were related to $^3J(H...H)$ in the ethyl group which is known to be positive [28].

Many transition metal complexes containing phosphine ligands have been studied by ^{31}P n.m.r. spectroscopy. Since most chemical changes considered in complexes involve the central atom, not phosphorus, variations in $\delta(^{31}P)$ are smaller. More use has been made of ^{31}P n.m.r. in studying coupling constants, in particular $^{1}J(M-P)$, because of the increased accuracy of direct measurement.

In a series of cis- and trans- isomers of the type $PtCl_2[PR_n(C_6H_5)_{3-n}]$ where R = alkyl and n = 1 - 3[17], it was found that $^{1}J(Pt-P)$ was always greater for the cis- compounds than for the corresponding trans- compound and that the ^{31}P resonance in the cis- isomer was upfield of that in the trans-. This was ascribed to the nature of the platinum-phosphorus bond. In addition to (Pt-P)π bonding from the in-plane dxy metal orbital, the cis- isomer could use both dxz and dyz for π bonding whereas the trans- isomer could only use dxz (if the x-axis is defined as the P-Pt-P direction). It was suggested that this would lead to a larger $^{1}J(Pt-P)$ for the cis- isomer and, because of increased electron density on phosphorus from back donation in the cis- form, an upfield shift in the ^{31}P resonance.

For the series trans-$[PtHX(PEt_3)_2]$ where X was an anionic ligand[18], correlations between $\delta(^{31}P)$ and both $\nu(Pt-H)$ and $^{1}J(Pt-P)$ were observed. The relationships were,

$$\delta(^{31}P) = -0.0536.\nu(PtH) + 95.33$$

$$^{1}J(PtP) = -26.85.\delta(^{31}P) + 2108$$

Of the ligands considered only the parameters for the cyano complex deviated from these relationships. It was suggested that this was a result of the CN ligand being the only one for which the Pt-L bond had a significant amount of π character.

Both Pidcock[19] and Heaton[20] have considered the value of $^{1}J(PtP)$, obtained from double resonance experiments, in relation to the other ligands present. They have discussed the magnitude of $^{1}J(Pt-P)$ in terms of the covalency of the Pt-P bond and the s-character of the platinum orbital used in the bond. If the cis/trans influence is considered to be a weakening of the cis/trans metal-ligand σ bond, then good correlations were obtained between $^{1}J(^{195}Pt-P)$ and the cis/trans influence series. Confirmation of this interpretation has been obtained from molecular orbital calculations on the trans influence of some square-planar platinum (II) complexes.[21]

Other workers[22,23] have also used ^{31}P n.m.r. spectroscopy to study the cis and trans influences of other ligands in complexes. It is pointed out[23] that, if a synergic mechanism exists, then $^{1}J(Pt-P)$, although it is just considered in terms of the s-character of the Pt-P bond, must also be affected by changes in the $(Pt-P)\pi$ bonding.

1.3. Some Bis-(triethylphosphine) Complexes of Platinum

The types of bis-(triethylphosphine) platinum complexes studied fall into three groups; those with Pt-SiH, Pt-GeH or Pt-CH bonds, those with PtH bonds and those with only platinum-halogen bonds. The first two groups of compounds are very easily studied by ^{1}H n.m.r. spectroscopy, usually having first order spectra, with couplings to ^{31}P and ^{195}Pt being observed. However, the spectra of many of these are similar and it is often impossible to be sure, from the ^{1}H spectrum alone, what the products of a reaction are. By investigating the ^{195}Pt and ^{31}P spectra, by double resonance methods it is possible to obtain information which greatly facilitates the identification of unknown compounds, as well as giving an insight into the nature of the platinum-silicon or platinum-germanium bond. With the six-coordinated platinum hydrides, because of their instability and in many cases almost identical ^{1}H spectra, double resonance was sometimes the only way of identifying the complexes in a mixture.

In all the complexes studied the ^{31}P and ^{195}Pt spectra were complicated by coupling with protons in the triethylphosphine groups. Nevertheless, couplings of ^{31}P and ^{195}Pt with other protons can usually be evaluated directly on a first-order basis from the ^{1}H spectra. For the double resonance experiments it was necessary to assume that the ^{31}P and ^{195}Pt spectra each consisted of a complex set of sub-spectra, the relative positions of

which were governed by first-order rules. Because of the complexity of the sub-spectra, it was often difficult to locate the exact centre of a group of lines and so estimated errors quoted in the tables of chemical shifts (Table 1.1) and coupling constants (Table 1.2) are quite large.

1.4. Double Resonance Studies of trans-$[PtCl(SiH_2Cl)(PEt_3)_2]$

This section covers in more detail the study of one complex before the general discussion of parameters which follows in section 1.5.

A schematic representation of the ^{195}Pt, ^{31}P and ^{1}H spectra for $PtCl(SiH_2Cl)(PEt_3)_2$ is given in Figure 1.1. In Figure 1.2 some of the 'decoupled' ^{1}H spectra are shown. Following the assumption above, the couplings of ^{31}P and ^{195}Pt with the ethyl protons have not been shown. Inclusion of these couplings would merely broaden the ^{195}Pt spectrum but would make the ^{31}P spectrum much more complex. By double irradiation at a, b, c or d the proton spectrum A, B, C or D is obtained. Complete collapse of the lines in the ^{1}H spectrum was not normally observed because of the width of the part of the ^{31}P or ^{195}Pt spectrum being irradiated. The frequencies required to obtain spectra B and D were then used to calculate $\delta(^{195}Pt)$ and $\delta(^{31}P)$ respectively. Details of these calculations are given in the Experimental Section. The value of $^{1}J(PtP)$ could then be calculated from $\nu(c) - \nu(d)$ or $\nu(a) - \nu(e)$.

Since irradiation at c led to collapse of the high frequency part of the ^{195}Pt satellites of the ^{1}H spectrum, then $\psi[^{1}J(PtP)] = \psi[^{3}J(PH)]$. Likewise from $^{1}H-\{^{31}P\}$ $\psi[^{1}J(PtP)] = \psi[^{2}J(PtH)]$ and so, if $^{1}J(PtP)$ is taken to be positive,[15,16] all three coupling constants are positive.

1.5. Discussion of n.m.r. Parameters

Chemical shifts and coupling constants are quoted in Tables 1.1 and 1.2 respectively.

^{195}Platinum Chemical Shifts. Although no satisfactory explanation of the observed ^{195}Pt chemical shifts has yet been put forward, there are certain systematic trends that can be used to predict chemical shifts of complexes, the ^{195}Pt spectra of which have not been studied.

The first point to note is that there are no simple additivity rules. A consequence of this is that ^{195}Pt chemical shifts for different isomers of the same compound are different. This may be seen from Table 1.1 to be so for the cis and trans forms of $PtCl_2(PEt_3)_2$, and for the two isomers of $PtBr_2HI(PEt_3)_2$.

It does appear however that, in any complex containing the grouping trans-[X-Pt-X] (X = Cl, Br, I), the effect of replacing one of the X ligands by H depends on X but is independent of the nature of the cis ligands, whether there are two or four of them.

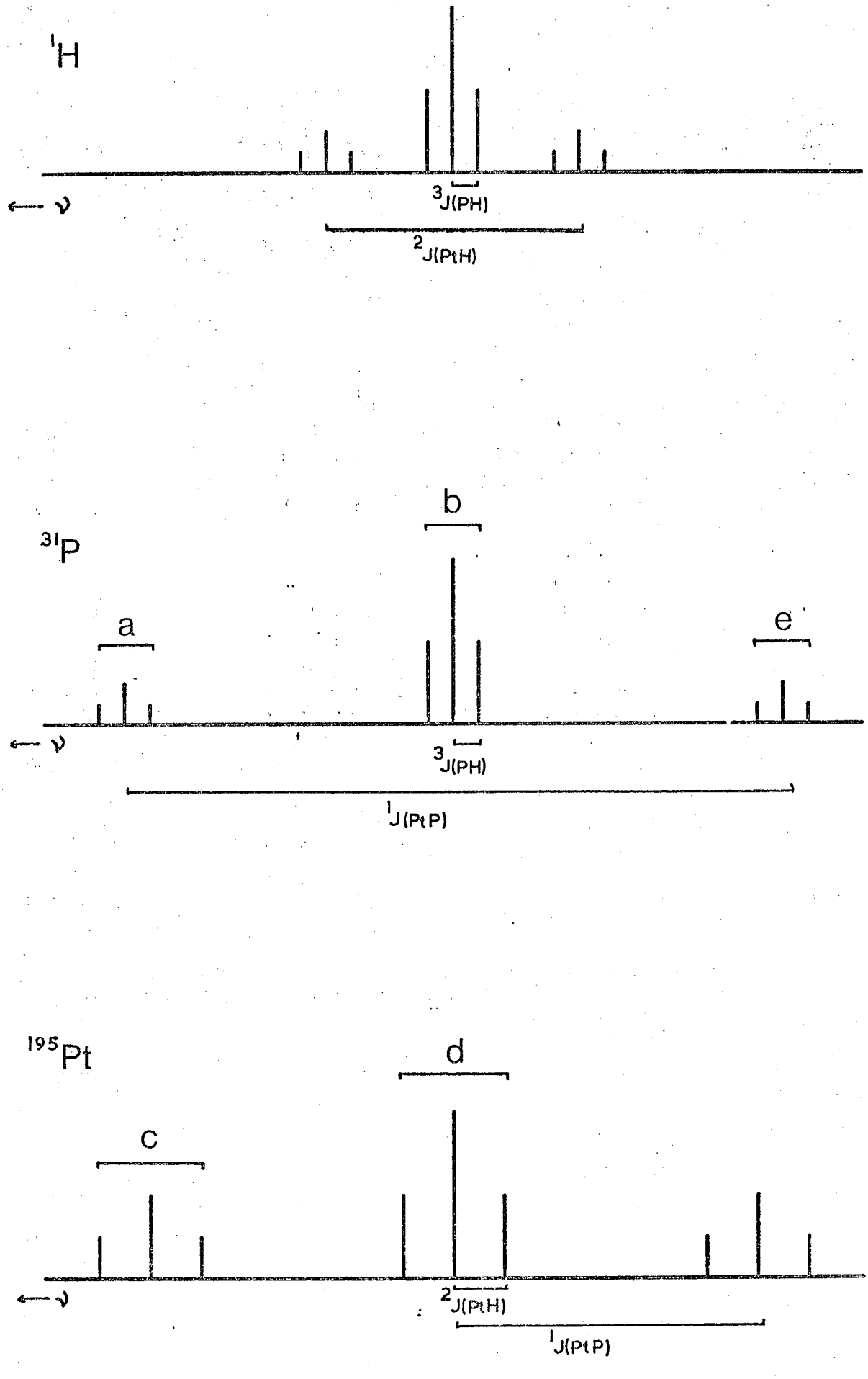


Fig. 1.1. N.M.R. spectra (not to scale) of t-$[PtCl(SiH_2Cl)(PEt_3)_2]$

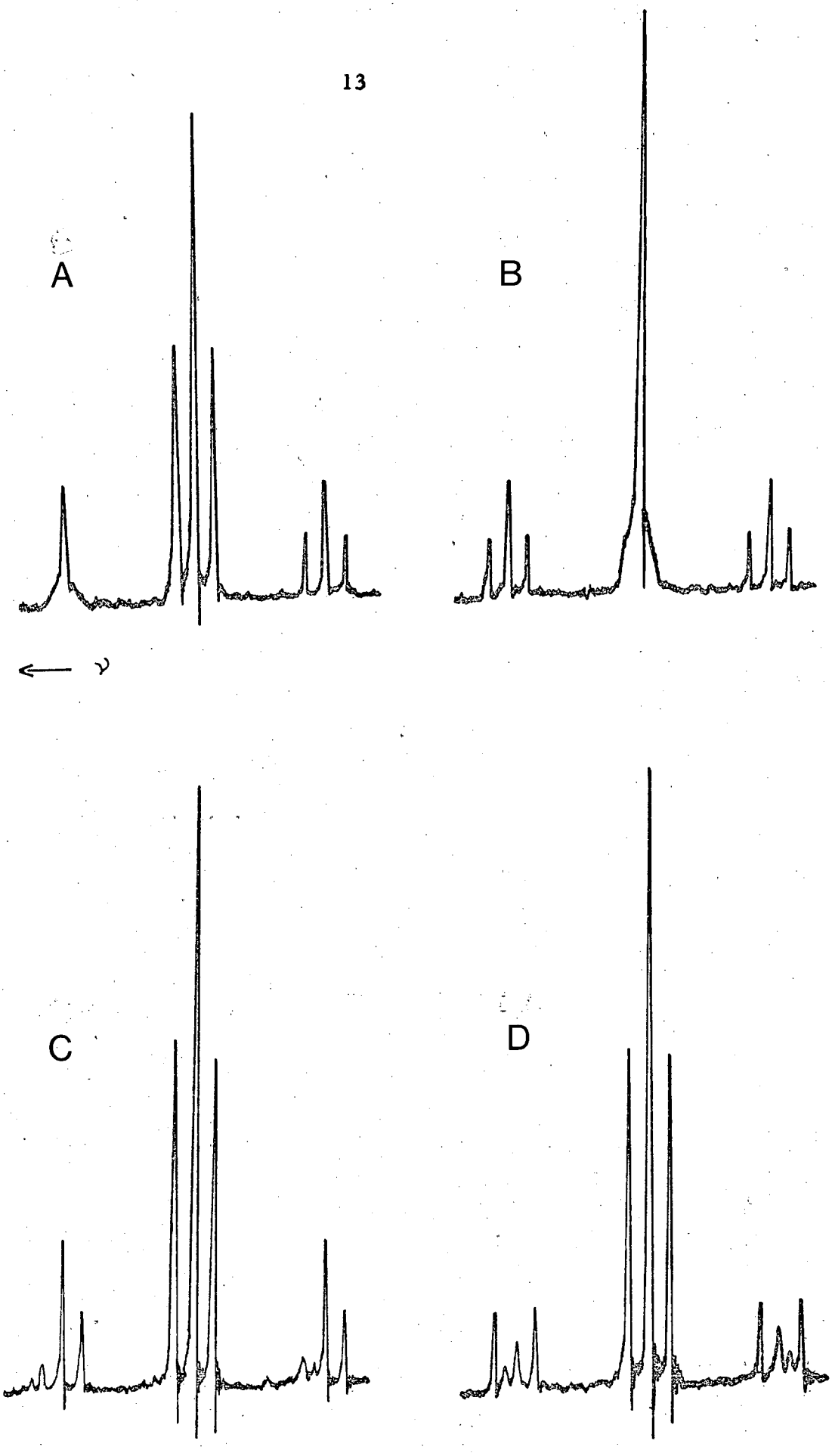


Fig. 1.2. ^{1}H n.m.r. spectra with ^{31}P and ^{195}Pt decoupling.

This is expressed graphically in Figure 1.3 for some of these complexes. Observed chemical shifts (marked +) are linked by continuous lines, representing changes of mutually trans (X,X) (X = Cl, Br or I) ligand pairs by (X, H). These lines are of three different gradients only, corresponding to the three different halogens. The dashed lines are extrapolations to unknown or unstudied compounds such as $PtI_4(PEt_3)_2$ or $PtBrCl_2H(PEt_3)_2$; these extrapolations may not predict chemical shifts exactly, but in view of the wide range of ^{195}Pt shifts, they should be close enough to the true values to be useful.

It can be seen that for both the six-coordinate and the four-coordinate complexes, the three lines corresponding to the three different halides meet at a common point (marked *) when extrapolated (dotted line in Figure). This observation is not necessarily of physical significance. However, if the ratios of the changes in chemical shifts for replacement of an (X,X) ligand pair by (X,H), and replacement of (X,H) by (H,H), is the same for each different X, then these two points represent the complexes $PtH_4(PEt_3)_2$ and $PtH_2(PEt_3)_2$. Other similar extrapolations would give chemical shifts for $PtH_2X_2(PEt_3)_2$ and $PtH_3X(PEt_3)_2$.

The influence of ligands other than halides on the ^{195}Pt chemical shifts can be seen from the series of complexes $PtIL(PEt_3)_2$, where the values change with the ligand L in the order $CH_3 > CN \gg H > SiH_3 > GeH_3 > I$. The relative positions of CH_3,

H and SiH_3 in this series is of interest, as silyl or, to a lesser extent, hydrido groups lead to low frequency resonances for ^{15}N,[24] ^{19}F,[25] ^{31}P,[26] and ^{77}Se[27] compounds, when compared with the resonances for equivalent organo derivatives.

The effects on the ^{195}Pt chemical shifts of changing substituents on silicon or germanium are, of course, relatively small. Nevertheless, the changes are sufficiently great to be useful diagnostically as, in general, replacement of one group by a more electronegative one leads to a high frequency shift. However, accurate prediction is difficult for unknown compounds, as the changes are certainly not additive, and sometimes vary in unexpected ways. The relative resonant frequencies of the four- and six- coordinate complexes with $-SiH_2C\equiv CH$ and $-SiH_2C\equiv CCF_3$ ligands exemplify this.

<u>^{31}P Chemical Shifts.</u> The first point to note is that free triethylphosphine resonates at -20.4 p.p.m.[17] This is to low frequency of any complexes studied here and due to deshielding of the phosphorus as a result of ligand-to-metal σ donation of electrons on formation of the bond. Since in all the complexes studied here, except one, the two triethylphosphine groups are mutually trans, any variations in ^{31}P chemical shift must be due to the influence of two or four cis ligands. That the number of other ligands coordinated to platinum is important is immediately evident from Table 1.1, for nearly all the six-coordinated complexes resonate

at lower frequencies than 85% H_3PO_4, whereas all the four-coordinated complexes resonate at higher frequencies.

The relative effects of cis ligands in raising the ^{31}P chemical shifts is $H > CH_3 \sim SiR_3 > GeR_3 > Cl > Br > I$, and within the SiR_3 group the order is $SiH_2F > SiHCl_2 > SiH_3 > SiH_2C{\equiv}CR \sim SiH_2Cl > SiH_2I$, although the changes within the latter series are relatively small. However, as with ^{195}Pt chemical shifts, the changes are sufficiently great for the ^{31}P shifts to be useful for identification purposes.

The relative arrangement, as well as number and type, of the cis ligands is of some importance in determining the ^{31}P chemical shift. This is demonstrated by the two isomers of $PtBr_2HI(PEt_3)_2$, which have a small, but significant, difference in shift.

<u>^{29}Si Chemical Shifts.</u> The ^{29}Si chemical shift has been determined for only one platinum complex $PtCl(SiH_2Cl)(PEt_3)_2$. The value found (-25.0 p.p.m. relative to tetramethylsilane) is about 12 p.p.m. to high frequency of that for free silyl chloride. Thus, on coordination to platinum, silicon is showing the same trend as phosphorus; deshielding by $M \leftarrow L$ σ donation leading to a shift of the resonance to higher frequency.

<u>Coupling Constants.</u> The values found for the platinum-phosphorus coupling constants in this series of compounds confirms the observations that have previously been made.[19,20] For

four-coordinated complexes, $^{1}J(^{195}Pt - ^{31}P)$ lies in the range +2100 Hz to +2800 Hz while for six-coordinated complexes it lies between +1450 Hz and +1800 Hz. This decrease corresponds to a decrease in the s-orbital character of the Pt-P bond on increase of coordination at platinum. Since in almost all the complexes considered the triethylphosphine ligands are mutually trans, the smaller variations in $^{1}J(Pt-P)$ can be attributed to cis- effects of the other ligands. The use of $^{1}J(Pt-P)$ as a measure of the cis/trans influence of other ligands has already been mentioned in section 1.2. Although an accurate list of cis- influences cannot be obtained because of the fairly large estimated errors in $^{1}J(Pt-P)$, general trends can be observed. The coupling constant for both four and six-coordinated complexes is larger for those with less halide and more hydride ligands. Also replacement of a hydride ligand by $-SiH_2X$ or GeH_2X leads to a decrease in the coupling constant. Probably the most marked decrease is found when a CN ligand is present; the smallest platinum-phosphorus coupling constant observed for four-coordinated complexes was +2100 Hz in $trans[Pt(CN)GeH_2Cl(PEt_3)_2]$. The following order of decreasing cis- effect can therefore be deduced:

$$CN > I > Br > Cl \sim SiH_2X \sim GeH_2X > H > CH_3$$

This corresponds well with other observed orders of the cis effect.[19,20,21,22]

In contrast to ^{1}J(Pt-P), the values of $^{1}J(^{195}Pt-^{1}H)$ are not dependent primarily on the coordination number of platinum, for the values are smaller for the six-coordinate mono-hydride complexes, but larger for the six-coordinate dihydride and larger still for nearly all the four-coordinated complexes. This will be discussed again in Chapter 2 and the values related to physical properties of the complexes. The only exception to the above order is trans-$[Pt(CN)H(PEt_3)_2]$ for which ^{1}J(PtH) is +807 Hz. This may be due to the very strong trans effect which the cyano ligand is known to have.[22] It has also been suggested that this is due to significant π-character of the Pt-CN bond.[18] Both ^{1}J(Pt-P) and ^{1}J(Pt-H) have been taken to be positive in all the compounds studied[15,16] and the signs of other coupling constants related to these.

Only one other one-bond coupling constant was determined; $^{1}J(^{195}Pt - ^{29}Si)$ in $PtCl(SiH_2Cl)(PEt_3)_2$ was found to be -1600 Hz. The reduced coupling constant, ^{1}K(Pt Si), is therefore $+3120 \times 10^{19}$ NA^{-2} cm^{-3}, compared with 2330×10^{19} NA^{-2} m^{-3} for ^{1}K(Pt P) in the same compound and 3360×10^{19} NA^{-2} m^{-3} in cis-$[PtCl_2(PEt_3)_2]$ where the ligand trans to the phosphine is also a chloride.

Most of the other reduced coupling constants in the compounds studied are positive over odd numbers of bonds, and negative over even numbers; this is consistent with a mechanism for coupling that is dominated by Fermi contact terms. There is however, one important exception. It has been noted that in the complexes

$PtX(MHYZ)(PEt_3)_2$ the magnitude of $^2J(^{195}Pt\,^1H)$ is greater with increasing substitution of halides for hydrides at M, and is much larger for M = Ge than for M = Si[29]. Values range from 434 Hz for a $GeHCl_2$ complex to less than 20 Hz in six-coordinate silyl acetylene complexes (see Chapter 3). With such a wide range of values, it was quite possible that the coupling constant would be found not to be always of the same sign. However, in every silyl or germyl complex the sign was found by $^1H-\{^{31}P\}$ double resonance experiments to be the same as that of $^1J(^{195}Pt\,^{31}P)$, and therefore positive, although in $Pt(CH_3)I(PEt_3)_2$ the equivalent coupling constant is negative. It would seem, therefore, that in the silyl and germyl complexes there is a positive contribution to the coupling constant which is greater than the negative Fermi contact term. This positive term is much larger when electron-withdrawing groups are attached to the silicon or germanium atom, larger for germanium than for silicon, and must also be smaller for six-coordinate complexes than for the corresponding four-coordinate complexes.

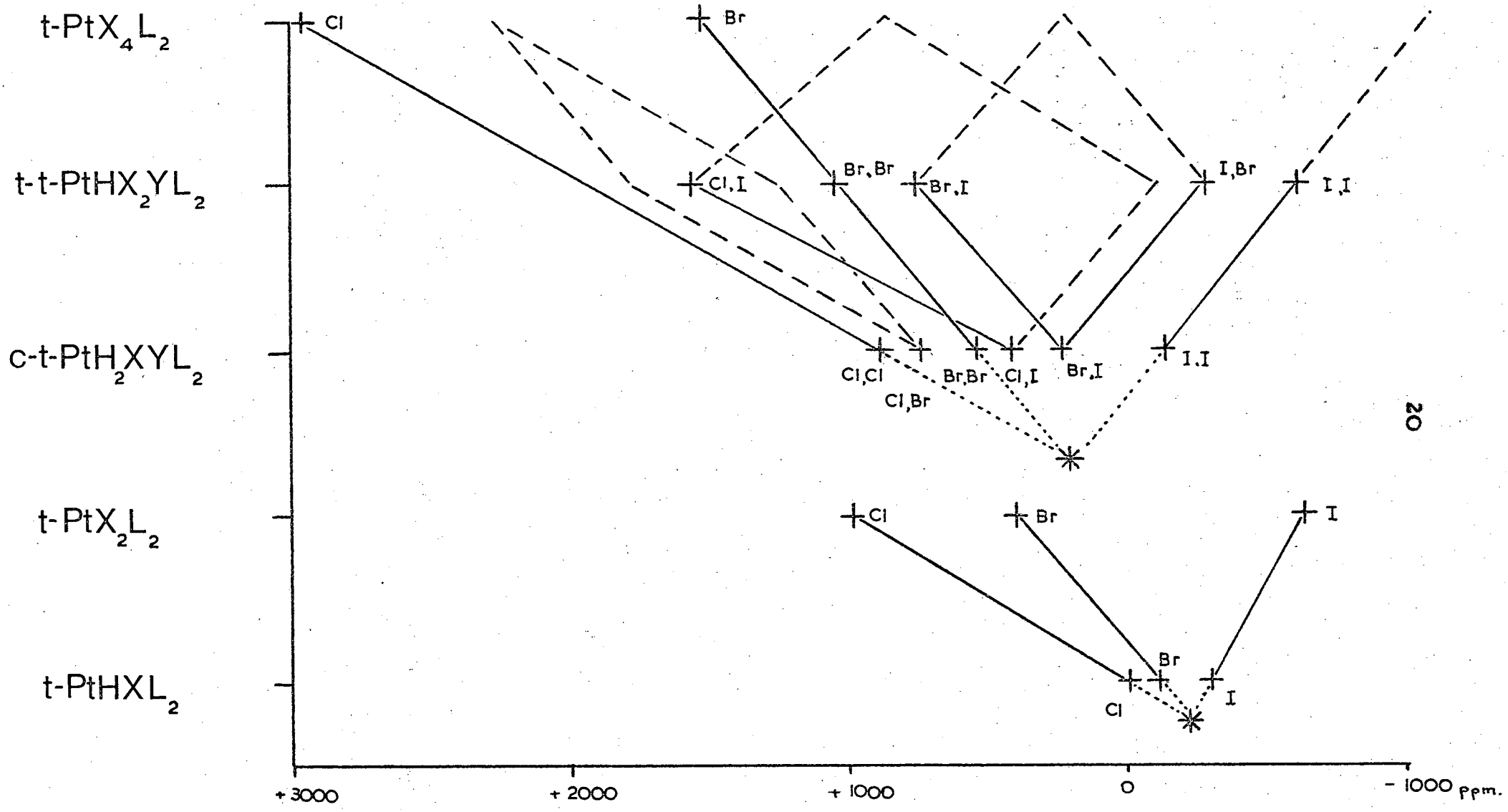


Fig. 1.3. ^{195}Pt Chemical shifts of some t-[$Pt(PEt_3)_2$-] complexes containing halogen and hydride ligands.

Table 1.1 ^{195}Pt and ^{31}P Chemical Shifts

No.	Compound	Ξ (^{195}Pt) in Hz[a]	δ(^{195}Pt) in p.p.m.[b]	Ξ ^{31}P in Hz[a]	δ(^{31}P) in p.p.m.[c]	Temperature	Solvent
1.	t-[Pt-$Cl_4(PEt_3)_2$]	21 454 721 (10)	+2925	40 480 925 (5)	+ 4.4	300	A
2.	t-[$PtBr_4(PEt_3)_2$]	21 424 410 (5)	+1508	40 480 354 (3)	- 9.7	300	A
3.	t-t-[$PtBr_3H(PEt_3)_2$]	21 414 081 (10)	+1026	40 480 835 (5)	+ 2.2	193	B
4.	t-t-[$PtHI_3(PEt_3)_2$]	21 377 980 (10)	- 662	40 480 082 (3)	-16.4	233	B
5.	t-t-[$PtCl_2HI(PEt_3)_2$]	21 424 984 (8)	+1535	40 480 923 (4)	+ 4.4	183	B
6.	t-t-[$PtBr_2HI(PEt_3)_2$]	21 408 032 (10)	+ 743	40 480 624 (5)	- 3.0	193	B
7.	c-t-[$PtBr_2HI(PEt_3)_2$]	21 398 838 (20)	+ 313	40 480 587 (8)	- 3.9	213	B
8.	t-t-[$PtBrHI_2(PEt_3)_2$]	21 385 293 (10)	- 320	40 480 316 (5)	-10.6	193	B
9.	c-c-t-[$PtCl_2H_2(PEt_3)_2$]	21 410 997 (10)	+ 881	40 481 241 (5)	+12.2	293	B
10.	c-c-t-[$PtBr_2H_2(PEt_3)_2$]	21 403 575 (10)	+ 534[d]	40 481 037 (5)	+ 7.2	253	B
11.	c-c-t-[$PtH_2I_2(PEt_3)_2$]	21 389 020 (7)	- 146[e]	40 480 689 (3)	- 1.4	253	B
12.	c-t-[$PtClBrH_2(PEt_3)_2$]	21 407 284 (30)	+ 708	40 481 144 (5)	+ 9.8	253	B

3.	c-t-$[PtClH_2I(PEt_3)_2]$	21	400	586 (30)	+ 395	40	480	976 (5)	+ 5.7	253	B
4.	c-t-$[PtBrH_2I(PEt_3)_2]$	21	396	569 (15)	+ 207	40	480	872 (5)	+ 3.1	253	B
5.	c-t-$[PtHI_2(SiH_2I)(PEt_3)_2]$	21	385	708 (25)	- 301	40	480	077 (5)	-16.5	253	A
6.	c-t-$[PtHI_2(SiH_2CCH)(PEt_3)_2]$	21	384	253 (10)	- 369	40	480	180 (5)	-14.1	243	A
7.	c-t-$[PtHI_2(SiH_2CCF_3)(PEt_3)_2]$	21	383	008 (10)	- 427	40	480	161 (8)	-14.5	243	A
8.	t-$[PtCl_2(PEt_3)_2]$[g]	21	412	376 (15)	+ 946	40	481	244 (5)	+12.3	300	A
9.	c-$[PtCl_2(PEt_3)_2]$[g]	21	401	000(30)	+ 414	40	481	097 (5)	+ 8.7	300	C
0.	t-$[PtBr_2(PEt_3)_2]$	21	400	386 (5)	+ 384	40	481	054 (3)	+ 7.6	300	A
1.	t-$[PtI_2(PEt_3)_2]$	21	377	753 (10)	- 673[h]	40	480	754 (3)	+ 0.2	300	A
2.	t-$[PtClH(PEt_3)_2]$[i]	21	392	145 (5)	0[j]	40	481	670 (3)	+22.8	293	C
3.	t-$[PtBrH(PEt_3)_2]$[i]	21	389	444 (10)	- 126	40	481	635 (3)	+22.0	293	A
4.	t-$[PtHI(PEt_3)_2]$[i]	21	385	195 (10)	- 325	40	481	527 (3)	+19.3	293	A
5.	t-$[Pt(CN)H(PEt_3)_2]$[i]	21	386	100 (10)	- 283	40	481	541 (5)	+19.6	300	B
6.	t-$[PtCl(SiH_3)(PEt_3)_2]$	21	387	770 (10)	- 205	40	481	450 (5)	+17.4	273	A
7.	t-$[PtCl(SiH_2F)(PEt_3)_2]$[k]	21	390	593 (10)	- 73	40	481	554 (3)	+20.0	233	A
8.	t-$[PtCl(SiH_2Cl)(PEt_3)_2]$[l]	21	389	360 (5)	- 130	40	481	428 (3)	+16.8	273	A

29.	t-[$PtCl(SiHCl_2)(PEt_3)_2$]	21	392	342 (5)	+ 9	40	481	468 (3)	+17.8	300	A
30.	t-[$PtCl(SiH_2C_5H_5)(PEt_3)_2$]	21	388	393 (10)	- 175	40	481	426 (5)	+16.8	273	D
31.	t-[$PtCl(GeH_2C_5H_5)(PEt_3)_2$]	21	389	983 (10)	- 101	40	481	285 (8)	+13.3	273	D
32.	t-[$PtCl(SiH_2CCH)(PEt_3)_2$]	21	388	141 (10)	- 187	40	481	420 (3)	+16.7	300	A
33.	t-[$PtCl(SiH_2CCCF_3)(PEt_3)_2$][m]	21	388	442 (4)	- 173	40	481	399 (5)	+16.1	300	A
34.	t-[$PtCl(GeH_2Cl)(PEt_3)_2$]	21	391	250 (10)	- 42	40	481	293 (5)	+13.5	300	A
35.	t-[$PtBr(SiH_2Br)(PEt_3)_2$]	21	387	898 (10)	- 199	40	481	296 (3)	+13.6	300	A
36.	t-[$Pt\text{-}Br(SiHBr_2)(PEt_3)_2$]	21	391	291 (5)	- 40	40	481	313 (3)	+14.0	300	A
37.	t-[$Pt(CH_3)I(PEt_3)_2$]	21	392	931 (10)	+ 37	40	481	164 (3)	+10.3	300	A
38.	t-[$PtI(SiH_3)(PEt_3)_2$]	21	383	421 (6)	- 408	40	481	217 (3)	+11.6	273	A
39.	t-[$PtI(SiH_2Cl)(PEt_3)_2$]	21	384	950 (10)	- 336	40	481	143 (5)	+ 9.8	300	A
40.	t-[$PtI(SiH_2I)(PEt_3)_2$]	21	385	685 (5)	- 302	40	481	028 (10)	+ 7.0	300	A
41.	t-[$PtI(SiHIMe)(PEt_3)_2$]	21	387	339 (20)	- 225	40	481	152 (10)	+10.0	300	E
42.	t-[$PtI(SiH_2C_5H_5)(PEt_3)_2$]	21	384	759 (15)	- 345	40	481	181 (10)	+10.7	273	D
43.	t-[$PtI(GeH_2C_5H_5)(PEt_3)_2$]	21	383	889 (10)	- 386	40	481	012 (5)	+ 6.6	273	D

4.	t-[PtI(SiHICCH)$(PEt_3)_2$]	21 386 830 (10)	- 249	40 481 039 (7)	+ 7.2	300	A
5.	t-[Pt(GeH_3)I$(PEt_3)_2$]	21 382 411 (10)	- 455	40 481 058 (5)	+ 7.7	273	A
6.	t-[Pt(CN)$SiH_2CN(PEt_3)_2$]	21 385 530 (10)	- 309	40 481 138 (3)	+ 9.7	233	C
7.	t-[Pt(CN)$SiH_3(PEt_3)_2$]	21 385 819 (10)	- 296	40 481 193 (5)	+11.0	198	C
8.	t-[Pt(CN)$GeH_3(PEt_3)_2$]	21 386 841 (10)	- 248	40 481 146 (5)	+ 9.9	300	A
9.	t-[Pt(CN)$GeH_2Cl(PEt_3)_2$]	21 386 900 (30)	- 236	n.o.	n.o.	300	A

Note: n.o. = not observed

Estimated standard deviations are quoted in parentheses. These do not include a possible error in the determination of the absolute frequencies of , at most, 4 Hz.

a. Resonant frequency at a polarising field strength such that the Me_4Si proton resonance is at exactly 100 MHz.

b. To high frequency of 0.5M $PtClH(PEt_3)_2$ in CH_2Cl_2 ($\Xi(^{195}Pt)$ = 21392145(5) Hz).

c. To high frequency of 85% H_3PO_4 ($\Xi(^{31}P)$ = 40480746(3) Hz).

d. 56 p.p.m. lower in C_6H_6/TMS

e. 57 p.p.m. lower in C_6H_6/TMS

f. 21 p.p.m. higher in CH_2Cl_2/TMS

g. See also reference 15.

h. 23 p.p.m. higher in CH_2Cl_2/TMS

i. See also reference 12

j. 36 p.p.m. lower in C_6H_6

k. $\Xi(^{19}F) = 94\ 077\ 089\ (3)$ Hz; $\delta(^{19}F) = -179.7$ p.p.m. to high frequency of CCl_3F. ($\Xi(^{19}F) = 94093963\ (3)$ Hz)

l. $\Xi(^{29}Si) = 19\ 866\ 685\ (10)$ Hz; $\delta(^{29}Si) = -25.0$ p.p.m. to high frequency of internal Me_4Si.

m. $\Xi(^{19}F) = 94\ 089\ 130\ (1)$ Hz; $\delta(^{19}F) = -51.3$ p.p.m. to high frequency of CCl_3F.

n. A = C_6H_6/TMS

B = CH_2Cl_2/TMS

C = CH_2Cl_2

D = CCl_3F/TMS

E = C_6H_6

Table 1.2. Coupling Constants (Hz)

No.	Compound	$^1J(PtP)$	$^1J(PtH)$	$^2J(PH)$	$^2J(PtH)$	$^3J(PH)$
1.	t-$[PtCl_4(PEt_3)_2]$	+1488 (10)	-	-	-	-
2.	t-$[PtBr_4(PEt_3)_2]$	+1480 (15)	-	-	-	-
3.	t-t-$[PtBr_3H(PEt_3)_2]$	+1578 (20)	+ 845 (2)	-5.0 (0.5)	-	-
4.	t-t-$[PtHI_3(PEt_3)_2]$	+1590 (20)	+ 784 (2)	-5.5 (0.5)	-	-
5.	t-t-$[PtCl_2HI(PEt_3)_2]$	+1675 (20)	+ 942 (2)	-4.0 (0.5)	-	-
6.	t-t-$[PtBr_2HI(PEt_3)_2]$	+1590 (20)	+ 870 (2)	-4.5 (0.5)	-	-
7.	c-t-$[PtBr_2HI(PEt_3)_2]$	n.o.	+ 831 (2)	-5.3 (0.5)	-	-
8.	t-t-$[PtBrHI_2(PEt_3)_2]$	+1600 (20)	+ 794 (2)	-5.3 (0.5)	-	-
9.	c-c-t-$[PtCl_2H_2(PEt_3)_2]$	+1775 (20)	+1178 (2)	-6.5 (0.5)	-	-
10.	c-c-t-$[PtBr_2H_2(PEt_3)_2]$	+1730 (20)	+1202 (2)	-6.3 (0.5)	-	-
11.	c-c-t-$[PtH_2I_2(PEt_3)_2]$	+1728 (20)	+1186 (2)	-5.8 (0.5)	-	-
12.	c-t-$[PtClBrH_2(PEt_3)_2]$	+1770 (20)	+1233 (2)	-7.0 (0.5)	-	-
		-	+1168 (2)	-7.0 (0.5)	-	-

13.	c-t-[$PtClH_2I(PEt_3)_2$]	+1729 (20)	+1240 (2)	-7.0 (0.5)	-	-
		-	+1132 (2)	-6.0 (0.5)	-	-
14.	c-t-[$PtBrH_2I(PEt_3)_2$]	+1710 (20)	+1220 (2)	-6.0 (0.5)	-	-
		-	+1176 (2)	-6.0 (0.5)	-	-
15.	c-t-[$PtHI_2(SiH_2I)(PEt_3)$]	+1700 (25)	+1160 (2)	-6.0 (0.5)	+59.2 (0.8)	+7.6 (0.5)
16.	c-t-[$PtHI_2(SiH_2CCH)(PEt_3)_2$][a]	+1690 (15)	+1126 (2)	-5.5 (0.5)	+19.0 (1)	+8.6 (0.5)
17.	c-t-[$PtHI_2(SiH_2CCCF_3)(PEt_3)_2$][b]	n.o.	+1113 (2)	-5.8 (0.3)	n.o.[c]	+7.7 (0.5)
18.	t-[$PtCl_2(PEt_3)_2$]	+2457 (30)	-	-	-	-
19.	c-[$PtCl_2(PEt_3)_2$][d]	+3560 (40)	-	-	-	-
20.	t-[$PtBr_2(PEt_3)_2$]	+2368 (15)	-	-	-	-
21.	t-[$PtI_2(PEt_3)_2$]	+2272 (20)	-	-	-	-
22.	t-[$PtClH(PEt_3)_2$]	+2730 (15)	+1275 (2)	-14.5 (0.3)	-	-
23.	t-[$PtBrH(PEt_3)_2$]	+2736 (20)	+1331 (2)	-13.7 (0.3)	-	-
24.	t-[$PtHI(PEt_3)_2$]	+2660 (20)	+1369 (2)	-13.3 (0.3)	-	-
25.	t-[$Pt(CN)H(PEt_3)_2$]	+2546 (25)	+ 807 (2)	-15.5 (0.5)	-	-

26.	t-[PtCl(SiH_3)(PEt_3)$_2$]	+2465 (20)	-	-	+ 36.5 (0.5)	+ 6.5 (0.5)
27.	t-[PtCl(SiH_2F)(PEt_3)$_2$][e]	+2515 (20)	-	-	+123.6 (0.5)	+ 5.0 (0.5)
28.	t-[PtCl(SiH_2Cl)(PEt_3)$_2$][f]	+2470 (15)	-	-	+117.6 (0.5)	+ 8.8 (0.3)
29.	t-[PtCl($SiHCl_2$)(PEt_3)$_2$]	+2400 (15)	-	-	+245.0 (0.5)	+10.4 (0.3)
30.	t-[PtCl($SiH_2C_5H_5$)(PEt_3)$_2$][g]	+2580 (30)	-	-	+ 72.6 (0.5)	+ 8.7 (0.3)
31.	t-[PtCl($GeH_2C_5H_5$)(PEt_3)$_2$][h]	+2495 (20)	-	-	+140 (0.5)	+ 8.4 (0.3)
32.	t-[PtCl(SiH_2CCH')(PEt_3)$_2$][i]	+2480 (20)	-	-	+ 43.5 (0.5)	+ 8.8 (0.3)
33.	t-[PtCl(SiH_2CCCF_3)(PEt_3)$_2$][j]	+2420 (10)	-	-	+ 45.0 (0.5)	+ 8.8 (0.3)
34.	t-[PtCl(GeH_2Cl)(PEt_3)$_2$]	+2410 (20)	-	-	+218.0 (0.5)	+ 7.4 (0.3)
35.	t-[PtBr(SiH_2Br)(PEt_3)$_2$]	+2440 (40)	-	-	+125.2 (0.5)	+ 9.4 (0.3)
36.	t-[PtBr($SiHBr_2$)(PEt_3)$_2$]	+2380 (20)	-	-	+244.4 (0.5)	+11.2 (0.3)
37.	t-[Pt(CH_3)I(PEt_3)$_2$]	+2750 (20)	-	-	- 80.6 (0.5)	+ 6.2 (0.3)
38.	t-[PtI(SiH_3)(PEt_3)$_2$]	+2465 (15)	-	-	+ 36.5 (0.5)	+ 6.5 (0.5)
39.	t-[PtI(SiH_2Cl)(PEt_3)$_2$]	+2430 (20)	-	-	+123.8 (0.5)	+ 9.6 (0.3)
40.	t-[PtI(SiH_2I)(PEt_3)$_2$]	+2390 (10)	-	-	+127.1 (0.5)	+ 9.6 (0.3)

41.	t-[PtI(SiHIMe)$(PEt_3)_2$][k]	+2530 (40)	-	-	n.o.	+13.8 (0.5)
42.	t-[PtI$(SiH_2C_5H_5)(PEt_3)_2$][l]	+2280 (30)	-	-	+ 78.4 (0.5)	+ 9.2 (0.3)
43.	t-[PtI$(GeH_2C_5H_5)(PEt_3)_2$][m]	+2480 (20)	-	-	-144.5 (0.5)	+ 8.2 (0.3)
44.	t-[PtI(SiHICCH')$(PEt_3)_2$][n]	+2380 (20)	-	-	+131.2 (0.5)	+12.7 (0.3)
45.	t-[Pt$(GeH_3)I(PEt_3)_2$]	+2440 (20)	-	-	+ 87.8 (0.5)	+ 5.9 (0.3)
46.	t-[Pt(CN)$SiH_2CN(PEt_3)_2$]	+2195 (20)	-	-	+ 27.8 (0.5)	+ 7.9 (0.3)
47.	t-[Pt(CN)$SiH_3(PEt_3)_2$]	+2328 (10)	-	-	+ 11.8 (0.5)	+ 6.1 (0.3)
48.	t-[Pt(CN)$GeH_3(PEt_3)_2$]	+2349 (12)	-	-	+ 46.5 (0.5)	+ 5.5 (0.5)
49.	t-[Pt(CN)$GeH_2Cl(PEt_3)_2$]	+2100 (80)	-	-	+140.2 (0.5)	n.o.

Notes: Estimated errors quoted in parentheses.

n.o. = not observed.

a = $^4J(HH')$ n.o.

b = Coupling with ^{19}F n.o.

c = < 14

d = Reference 15

e = $^2J(FH)$ + 52.2 (0.5), $^2J(PtF)$ + 358.5 (0.5), $^3J(PF)$ + 9.5 (0.5)

f = $^{1}J(SiH)$ - 204 (2), $^{1}J(PtSi)$ - 1600 (100), $^{2}J(PSi)$ + 18 (3)

g = $^{3}J(HSiCH) \pm 2.8$ (0.5)

h = $^{3}J(HGeCH)$ n.o.

i = $^{4}J(PtH)$ - 15.4 (0.7), $^{4}J(HH')$ - 1.4 (0.3), $^{5}J(PH')$ n.o.

j = $^{5}J(PtF)$ + 23.7 (0.8), $^{5}J(HF) \pm 2.2$ (0.3), $^{6}J(PF)$ n.o.

k = $^{4}J(PtH) \pm 29.3$ (0.5)

l = $^{3}J(HSiCH) \pm 2.9$ (0.5)

m = $^{3}J(HGeCH)$ n.o.

n = $^{4}J(HH')$ (-) 1.3 (0.4)

CHAPTER 2

HYDRIDE COMPLEXES OF SIX-COORDINATED PLATINUM

2.1. Introduction

Many examples are known of monohydride complexes of 4-coordinated platinum; a large number are crystalline solids stable at and above room temperature. Hydrides of 6-coordinated platinum, however, are not so well characterised. Monohydride complexes have been isolated as intermediates in the oxidative addition of silyl and germyl halides to trans-$[PtI_2(PEt_3)_2]$[29]; at 258K complexes of the type cis-trans-$[PtHI_2(SiH_2I)(PEt_3)_2]$ were observed and isolated but on standing they decomposed by elimination of HI or MH_2XI (M = Si, Ge; X = Cl, I). When $PtClH(PEt_3)_2$ was treated with excess GeH_3Cl another series of six-coordinated monohydride complexes was formed[30]. Trans-$[Pt(GeH_2Cl)_3H(PEt_3)_2]$, and other complexes with further halogen substitution on germanium, have been detected and characterised by ^1H n.m.r. spectroscopy. Another six-coordinated complex with a Pt-Ge bond has been isolated by Glockling[36]. Treatment of $[(Ph_2P.(CH_2)_2.PPh_2)Pt(GeMe_3)(PEt_3)]Cl$ with anhydrous HCl in benzene gave a white precipitate of $[(Ph_2P.(CH_2)_2.PPh_2)PtCl(GeMe_3)H(PEt_3)]Cl$. When it was dissolved in methanol it broke down to give Me_3GeCl and a four-coordinated ionic platinum hydride.

A solid adduct of HCl with $PtClH(PEt_3)_2$ has been described as a dihydride of 6-coordinated platinum[31] on the basis of its i.r. spectrum, C,H analysis and its behaviour as a non electrolyte in nitrobenzene solution. The latter suggests that the dihydride

complex was $PtCl_2H_2(PEt_3)_2$ rather than $[PtClH_2(PEt_3)_2]Cl$. This same 6-coordinate dihydride complex was formed when solid trans-$[PtCl(SiH_2Cl)(PEt_3)_2]$ was treated with liquid HCl.[29] Trichlorosilane was evolved and a solid, consisting of $PtCl_2H_2(PEt_3)_2$ and $PtCl(SiCl_3)(PEt_3)_2$, left. The complexes were identified by their i.r. spectra.

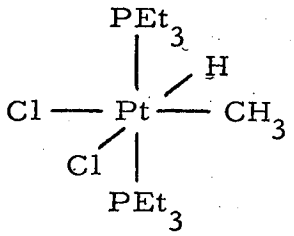
Other platinum dihydrides have been postulated. Complexes which were originally described as $Pt(PPh_3)_n$ (n = 3,4)[32] were later postulated to be the dihydride complexes of platinum, $PtH_2(PPh_3)_n$ (n = 2,3,4).[33] The evidence for these was i.r. spectroscopy, C,H analyses, titration with bromine water and the reaction with CCl_4 to produce $CHCl_3$. These complexes, however, have now been shown not be be platinum hydrides; $PtH_2(PPh_3)_n$ (n = 3,4) were in fact the original non-hydride platinum phosphine complexes[34] and $PtH_2(PPh_3)_2$ was shown to be $Pt(CO_3)(PPh_3)_2$[35]. $PtCl_2H_2(PPh_3)_2$ has also been reported as an adduct of HCl with $PtClH(PPh_3)_2$[37]. The solid, which was characterised by C,H,P analysis and i.r. spectroscopy, lost HCl slowly and has now been shown[38] to be another crystalline form of $PtClH(PPh_3)_2$. The only other reported dihydride is PtH_2(1-ethynylcyclohexanol)$_2$ $(PPh_3)_2$[47]; this compound had a ^1H resonance at 22.88 τ and, in the mass spectrum, gave weak peaks at 196, 197, 198 assigned to the PtH_2^+ ion.

Other six-coordinated platinum hydride complexes have been

postulated although they have not been isolated.[39-42] In the isotopic exchange reaction,[43]

$$trans\text{-}[PtClH(PEt_3)_2] + D_2O \xrightarrow{Cl^-} trans\text{-}[PtClD(PEt_3)_2] + HDO$$

an intermediate of the form $PtCl_2DH(PEt_3)_2$ has been proposed. Also, in the study of the kinetics of the reaction of trans-$[Pt(CH_3)X(PEt_3)_2]$ (X = Cl, I) with HCl in methanol[44] to give trans-$[PtClX(PEt_3)_2]$, the intermediate



has been proposed. This then lost CH_4 to give the observed product.

In this chapter a series of mono- and dihydride complexes of 6-coordinated platinum, of general formulae $PtHXY_2(PEt_3)_2$ and $PtH_2XY(PEt_3)_2$ (X, Y = halogen), is described. The products have been characterised by ^1H n.m.r. spectroscopy, with extensive use being made of the heteronuclear double resonance techniques described in Chapter 1. These techniques have been used elsewhere in the study of complexes of platinum.[14,45]

2.2. Dihydride complexes

When equimolar proportions of HX and trans-$[PtHX(PEt_3)_2]$

(X = Cl, Br or I) were allowed to react together in methylene chloride in a sealed tube at 253K, changes in the PtH resonance and colour changes (X = Br, I) showed that a chemical change had occurred. The triplet PtH resonance and the values of $^{1}J(^{195}Pt\ ^{31}P)$ imply that the phosphorus atoms are mutally trans in the reaction product (Figure 2.1); the ^{195}Pt resonance showed the pattern of a triplet of triplets expected for a dihydride complex, with one of the triplet splittings equal to $^{1}J(^{195}Pt\ ^{1}H)$ as measured directly from the ^{1}H spectrum. All the coupling constants are reduced in magnitude from their values in the parent complexes of 4-coordinated platinum, which is consistent with the increase in coordination number of the metal atom.

Reaction of HX with trans-$[PtHY(PEt_3)_2]$ (X, Y = Cl, Br, I; X ≠ Y) at 183K gave as the major product a compound with two PtH resonances. Heteronuclear decoupling and the determination of $\delta(^{195}Pt)$ showed that both resonances were associated with protons bound to the same platinum atom. When this solution was allowed to warm to 253K, resonances due to $PtH_2X_2(PEt_3)_2$ and $PtH_2Y_2(PEt_3)_2$, weak in the initial spectra at 183K, increased in relative intensity until they were comparable with the other two PtH resonances. These results are consistent with initial formation of $PtH_2XY(PEt_3)_2$, and subsequent 'scrambling' of halogens on a very roughly statistical basis:

$$2PtH_2XY(PEt_3)_2 \rightleftharpoons PtH_2X_2(PEt_3)_2 + PtH_2Y_2(PEt_3)_2.$$

The ^1H n.m.r. spectrum of the three products from the reaction of HCl with $PtHI(PEt_3)_2$ is shown in Figure 2.2. If this interpretation is correct, the hydride ligands in the mixed species must be mutually cis; if they were trans, they would be equivalent. The coupling $^2J(HPtH)$ was not observed, even at 183K, although splittings of the order of 0.5 - 1.0 Hz would have been detected. Thus the stereochemistry of these dihydride complexes is established.

The reaction between HX and trans-$[PtHX(PEt_3)_2]$ is very rapid; n.m.r. spectra run after about a minute at 183K showed that extensive reaction had occurred. The spectra are sharp at room temperature, showing that there is no rapid exchange with free HX, but over a few minutes H_2 is evolved irreversibly; the order of stability is $Cl \gg Br > I$, which is the order of increasing trans influence. By removal of the solvent at 253K cis-cis-trans-$[PtH_2X_2(PEt_3)_2]$ (X = Cl, Br) was isolated, both being white solids. They were stable enough to be characterised more fully by C, H analysis and infrared and Raman spectroscopy (Table 2.2). For X = I an orange solid was obtained but it decomposed too readily for further study.

An attempt was made to discover whether the initial addition was cis or trans by treating trans-$[PtHX(PEt_3)_2]$ with DY

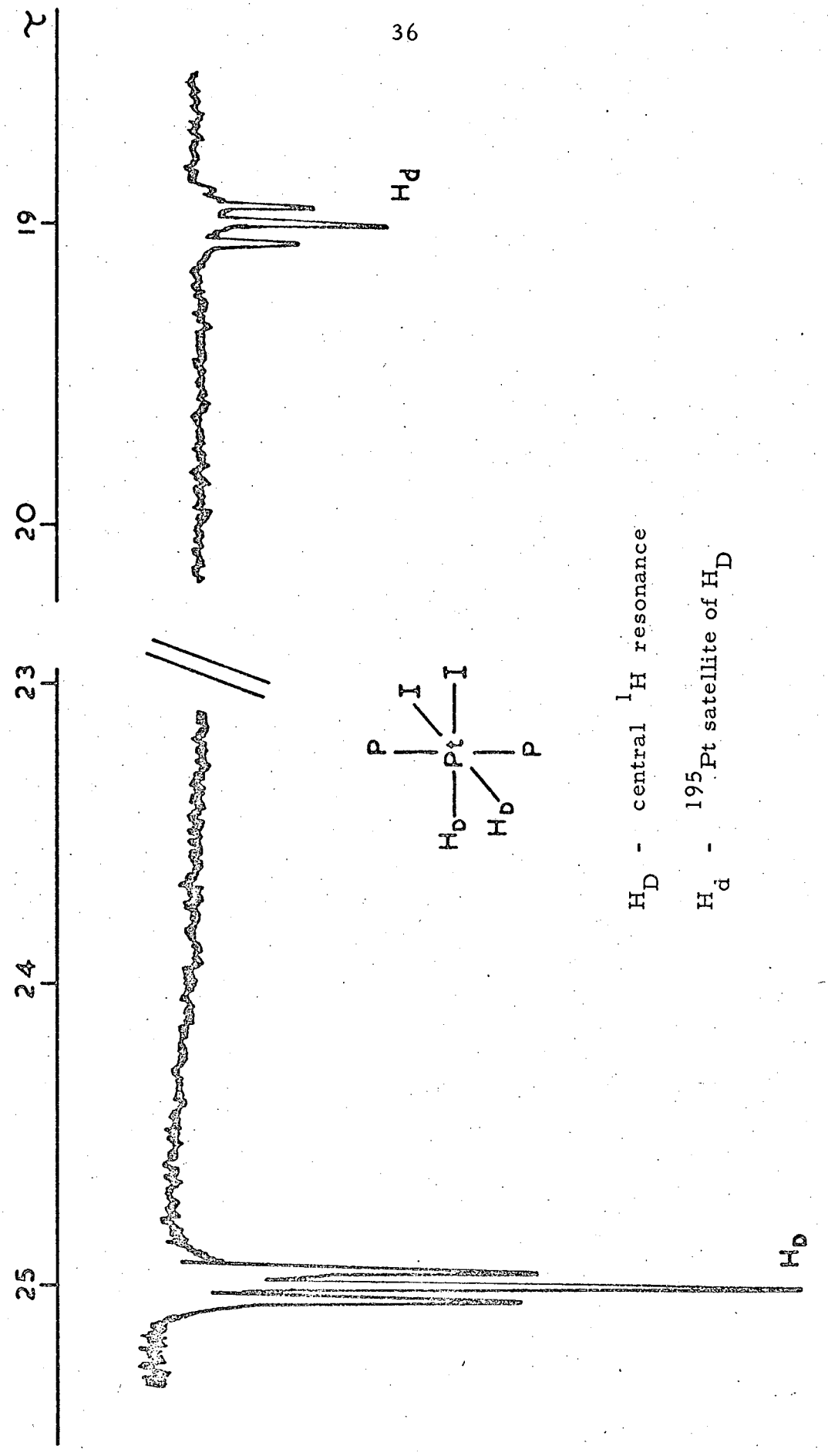


Fig. 2. 1. ^1H n.m.r. spectrum of Pt-H in c-c-t-$[PtH_2I_2(PEt_3)_2]$

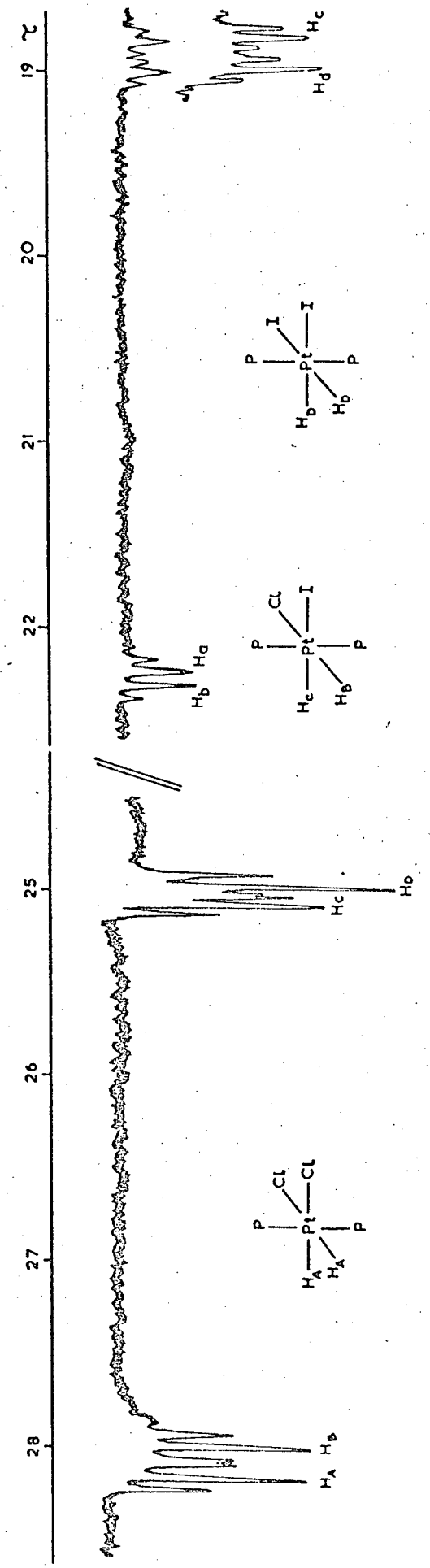


Fig. 2.2. ^1H n.m.r. spectrum of Pt-H in c-c-t-$[PtH_2XY(PEt_3)_2]$

Table 2.2. Vibration Spectra

cis-cis-trans-$[PtCl_2H_2(PEt_3)_2]$		cis-cis-trans-$[PtBr_2H_2(PEt_3)_2]$		
IR[a]	Raman[b]	IR[a]	Raman[b]	Assignments
	2973w		2971w	
	2949m		2951m	
	2907m		2913s	ν(CH)
	2888w		2886w	
2263m, sh.	2269(2)s	2252s	2254(2)s	
2251s	2264(2)m	2243s	2244(2)s	ν(PtH)[c]
	1459w		1455m	
	1427w		1426w	δ(CH)
1412m	1417w	1412m	1415w	
	1270w	1272s	1271s	
1263s		1260s		ν(CC)
1249s	1243w	1251s	1240w	
1048s	1055w	1050s	1055m	
		1046s		
1003s	1003w	1006s	1002m	
	987w		990w	
901w		903w		
892w		895w		
821s	823m	810s	809s	δ(PtH)
	784m		780m	
768 v.s, br.	775m	768 v.s.	765m	
	752w		745w	

	737v.w.			
701s	700m	700s	698s	
632m	638m	632m	638s	
577m	576m	548m	548s	δ(PtH)
	527v.w.			
435w		438w		
402m	404m	402m	404m	ν(PtP)
395w, sh.	394m		394m	
359 v.w.	364s	358w	364s	
348w		347w		
275m	284v.s.		284m	ν(PtX)
254s	256m	268w		
			222m	
	182v.s, br.		192v.s.	+δ(PtX)
	121v.s.		165m	+lattice modes

Note: a = Solid (Nujol mull)

b = Solid

c = cis-cis-trans-$[PtH_2I_2(PEt_3)_2]$ 2210 (νPtH)

trans-$[PtHI_3(PEt_3)_2]$ ca. 2210 (νPtH)

Solutions of the complexes cis-cis-trans-$[PtH_2X_2(PEt_3)_2]$ (X = Cl, Br, I) gave 2256, 2232 and 2217 cm^{-1} respectively for ν(PtH)

at 183K, but even at this temperature the first spectrum obtained showed the presence of H trans to both X and Y. This implies that reversible trans addition is not the only process going on under these conditions; H/D scrambling in the mixed species seems to be faster than the X/Y scrambling. From this evidence it is not possible to conclude whether the initial addition of HX is cis or trans.

2.3. Monohydride complexes

When HI was allowed to react with trans-$[PtI_2(PEt_3)_2]$ in methylene chloride at 293K, the solution darkened immediately; at 253K a strong Pt<u>H</u> resonance was obtained, and heteronuclear double resonance showed the presence of one hydride and two mutually trans P-ligands bound to platinum. At higher temperatures the Pt<u>H</u> resonance collapsed, but it reappeared on cooling again; presumably rapid exchange with free HI occurs at the higher temperatures. In the analogous bromide system, a similar Pt<u>H</u> resonance was found, but only at temperatures below 200K; in solutions containing comparable concentrations of starting materials, the Pt<u>H</u> resonance was much weaker for the bromide than for the iodide. Even at temperatures as low as 173K we were unable to detect a Pt<u>H</u> resonance in solutions containing HCl and trans-$[PtCl_2(PEt_3)_2]$.

The reaction between HX and trans-$[PtX_2(PEt_3)_2]$ therefore

appears to be an equilibrium, fast on the n.m.r. time scale at room temperature; the rates and instability constants decrease in the order X = (Cl >)Br > I:

$$PtHX_3(PEt_3)_2 \rightleftharpoons PtX_2(PEt_3)_2 + HX.$$

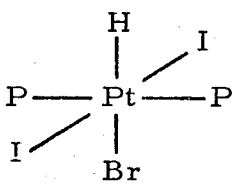
The change in equilibrium constant with halogen may be related to bond energies. Values for Pt-X bonds are not very reliable, but E(Pt-X) does not appear to be as sensitive to X as is E(H-X), which decreases markedly in the order Cl > Br > I. The equilibrium concentration of $PtCl_3H(PEt_3)_2$ might therefore be small. Even with a three-fold excess of HCl there was no detectable Pt<u>H</u> resonance of this species at 173K, but it is not possible to say whether this failure is due to an unfavourable equilibrium constant, to too fast a reaction, or to a combination of the two.

Reactions between HX and trans-$[PtY_2(PEt_3)_2]$ led ultimately to halogen exchange but the resonance due to the species formed initially could be observed at low temperatures; in contrast to the behaviour of $PtH_2XY(PEt_3)_2$, halogen scrambling only occurred to a significant extent when the solution was allowed to warm from 183 to 253K. This may be related to the high trans activating effect of H as a ligand. Furthermore, the rate of 'scrambling' in the monohydride system appears to decrease in the order Cl > Br > I. The ultimate products, too, are not random,

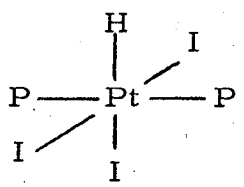
but are those in which H is trans to the lightest halogen present; this is established from the ^1H chemical shift, which depends almost entirely on the trans ligand, and may be interpreted in terms of the weakening of the PtH bond by the trans influence of the heavier halogens.

Since ^1H resonance of the initial product could be recorded before halogen exchange led to the formation of the most stable species, it was possible to show by reaction between HX and trans-$[PtY_2(PEt_3)_2]$ that the initial addition and elimination are trans. The halogen scrambling that occurs at higher temperatures must involve either cis elimination of HY from the monohydride adduct, or some quite different process, such as ionic exchange of halogen.

These effects are illustrated in the spectra of the mixed bromo-iodo complexes. When X = Br, Y = I, the product formed at 183K is (I):



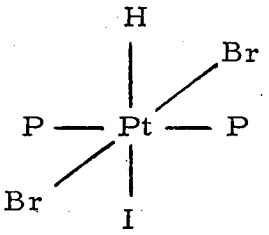
I



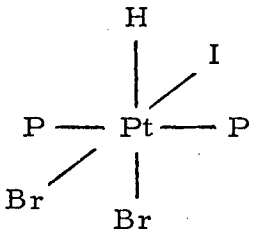
II

On warming, some halogen exchange occurs, but (I) is thermodynamically stable and persists as the main product at 253K. A

small amount of product (II) is also present at that temperature. When X = I, Y = Br, the initial product (III) has H trans to I; scrambling leads to the formation of products with H trans to Br, identified by their n.m.r. parameters (particularly ^{195}Pt chemical shift) as $PtBr_2HI(PEt_3)_2$ (IV, the major product) and $PtBrHI_2(PEt_3)_2$ (I).



III



IV

In the reaction of HCl with any dihalide, the lability of the adduct formed made it impossible to establish that initial trans addition had occurred. Addition of HBr or HI to trans-$[PtCl_2(PEt_3)_2]$ gave initial adducts with H trans to the heavier halogen. With HBr, scrambling was so rapid that not all the n.m.r. parameters of this initial product could be recorded, but the ^1H chemical shift showed that trans addition had occurred. With HI the spectrum of $PtHI_3(PEt_3)_2$ appeared as the solution warmed and the spectrum of $PtCl_2HI(PEt_3)_2$ decayed; ultimately this spectrum also diminished in intensity, the colour of the solution grew lighter, and all Pt<u>H</u> resonances disappeared.

Removal of the solvent from a solution of trans-

$[PtHI_3(PEt_3)_2]$ gave a red solid but this was too unstable to be characterised further.

2.4. Reaction of X_2 with trans-$[PtHX(PEt_3)_2]$

Addition of X_2 to trans-$[PtHX(PEt_3)_2]$ under the conditions described above might have been expected to give similar monohydride complexes. When X = Cl, however, the only Pt<u>H</u> resonance observed at 253K after reaction at that temperature was due to $PtCl_2H_2(PEt_3)_2$. Irradiation of ^{195}Pt while observing the Pt satellites of the methylene protons of the Et_3P groups showed that trans-$[PtCl_4(PEt_3)_2]$ had also been formed; the yellow colour of the solution was consistent with the presence of this compound. Reaction had occurred according to the equation:

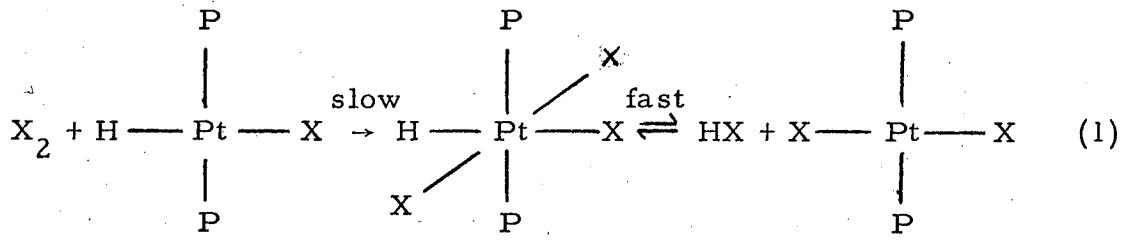
$$2PtClH(PEt_3)_2 + 2Cl_2 \rightarrow PtCl_2H_2(PEt_3)_2 + PtCl_4(PEt_3)_2$$

Reaction at 183K did not reveal the presence of $PtCl_3H(PEt_3)_2$ as an intermediate at this temperature.

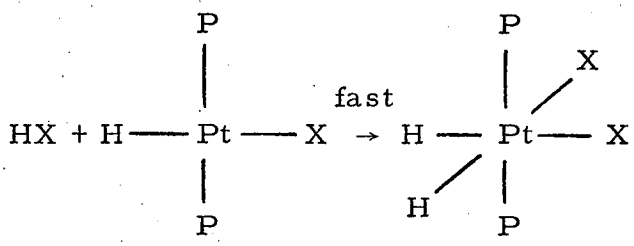
Reaction between Br_2 and trans-$[PtBrH(PEt_3)_2]$ gave similar products; the presence of $PtBr_4(PEt_3)_2$ in the red solution was confirmed in the same way. (Spectra of $PtCl_4(PEt_3)_2$ and $PtBr_4(PEt_3)_2$ had previously been obtained using samples prepared from the appropriate halogen and platinum dihalide.) The ^1H resonance spectrum of the products of the reaction between I_2 and trans-$[PtHI(PEt_3)_2]$ at 253K, however, showed that both $PtH_2I_2(PEt_3)_2$ and $PtHI_3(PEt_3)_2$ were present; it was neither

possible to detect the presence of any additional platinum complex of Et_3P, nor to prepare a sample of $PtI_4(PEt_3)_2$ from I_2 and $PtI_2(PEt_3)_2$.

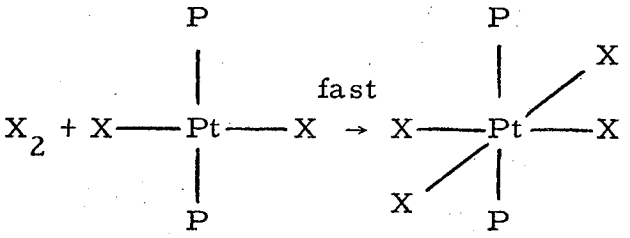
These observations are consistent with the following reaction scheme:



(1)



(2)



(3)

For X = Cl or Br, the equilibrium in step (1) is known from above to be fast, as are the subsequent reactions (2) and (3). If the formation of the monohydride in step (1) is slow, the spectrum of this compound will not be observed. When X = I, since the compound $PtI_4(PEt_3)_2$ is not readily formed from I_2 and trans-$[PtI_2(PEt_3)_2]$, the equilibrium in step (1) will be maintained, giving a finite concentration of $PtHI_3(PEt_3)_2$. Some HI can undergo

further reaction (2) giving $PtH_2I_2(PEt_3)_2$. To determine the mode of addition, trans-$[PtHX(PEt_3)_2]$ has to be treated with XY or YZ, and the monohydride intermediate isolated. However, since step (1) and subsequent scrambling of products are fast this was not possible. Reaction of ICl with trans-$[PtHI(PEt_3)_2]$ at 183K gave the three possible dihydrides, but no monohydride.

2.5. N.M.R. parameters

All the n.m.r. parameters measured are presented in Table 2.1.

The chemical shifts of all the PtH protons in the 6-coordinated platinum complexes are to low frequency of those of the 4-coordinated analogues with the same ligand trans to H; the values for the latter are included for comparison in Table 2.1. The chemical shift of the PtH within a group of similar compounds is determined mainly by the halogen in the trans position; changing halogens in the cis position has only a small effect. However, replacing a cis proton by a halogen (i.e. changing from dihydride to monohydride) changes the proton chemical shift substantially.

Variations in the ^{195}Pt and ^{31}P chemical shifts have been considered in Chapter 1. Several interesting trends should, however, be mentioned here. Both $\delta(^{31}P)$ and $\delta(^{195}Pt)$ are in all cases shifted to higher frequency by substitution of lighter for heavier halogens. $\delta(^{31}P)$ for each of the monohydride complexes

Table 2.1. N.M.R. parameters of platinum hydride complexes

Compound	τ	$\delta(^{31}P)^a$	$\delta(^{195}Pt)^b$	$^1J(PtH)$	$^1J(PtP)$	$^2J(PH)$	Temp. observed	Colour
$[PtHI_3(PEt_3)_2]$	+26.41	-16.4	- 662	+ 784	+1590	- 5.5	233K	Deep red
t-$[PtBrHI_2(PEt_3)_2]$	+28.75	-10.6	- 320	+ 794	+1560	- 5.5	193K	Orange-red
t-$[PtBr_2HI(PEt_3)_2]$	+28.53	- 3.9	+ 313	+ 831	ca.+1600	- 5.5	213K	Red
t-$[PtBr_2HI(PEt_3)_2]$	+26.41	- 3.0	+ 743	+ 870	+1590	- 4.5	193K	Red
$[PtBr_3H(PEt_3)_2]$	+28.33	+ 2.2	+1026	+ 845	+1578	- 5.0	193K	Yellow-orange
t-$[PtCl_2HI(PEt_3)_2]$	+26.48	+ 4.4	+1535	+ 942	+1675	- 4.0	183K	Light red
t-$[PtCl_2HBr(PEt_3)_2]$	+28.18	n.o.	n.o.	+ 944	n.o.	n.o.	183K	Yellow
c-t-$[PtH_2I_2(PEt_3)_2]$	+25.00	- 1.4	- 146	+1186	+1738	- 5.8	253K	Yellow
t-$[PtBrH_2I(PEt_3)_2]$	+26.82[c] +25.00[d]	+ 3.1	+ 207	+1176[c] +1220[d]	+1710	- 6.0[c] - 6.0[d]	253K	Yellow
t-$[PtClH_2I(PEt_3)_2]$	+28.03[c] +25.09[d]	+ 5.7	+ 395	+1132[c] +1240[d]	+1732	- 7.0[c] - 6.0[d]	253K	Pale yellow
c-t-$[PtBr_2H_2(PEt_3)_2]$	+26.88	+ 7.2	+ 534	+1204	+1710	- 6.3	253K	Pale yellow

-t-$[PtClBrH_2(PEt_3)_2]$	+28.09[c] +27.00[d]	+ 9.8	+ 708	+1168[c] +1234[d]	+1770	- 7.0[c] - 7.0[d]	253K	V.pale yellow
-c-t-$[PtCl_2H_2(PEt_3)_2]$	+28.17	+12.2	+ 881	+1176	+1769	- 6.5	293K	Colourless
-$[PtHI(PEt_3)_2]$[e]	+22.65	+19.3	- 325	+1369	+2660	-13.3	293K	V.pale yellow
-$[PtBrH(PEt_3)_2]$[e]	+25.55	+22.0	- 126	+1331	n.o.	-13.7	293K	Colourless
-$[PtClH(PEt_3)_2]$	+26.80	+22.8	0	+1275	+2730	-14.5	293K	Colourless
Estimated errors	± 0.03	± 0.3	± 1	± 2	±20	± 0.5	-	-

Note:

n.o.	=	not observed
a	=	p.p.m. to high frequency of external 85% H_3PO_4
b	=	p.p.m. to high frequency of external 0.5M trans-$[PtClH(PEt_3)_2]$ in CH_2Cl_2
c	=	H trans to lighter halogen
d	=	H trans to heavier halogen
e	=	Solvent C_6H_6. All others in CH_2Cl_2

is to low frequency of the range found for the dihydrides. In contrast, the ranges of ^{195}Pt shifts are centred around the same value, but variations in shifts for monohydrides are greater than those for the dihydrides.

The magnitudes of the coupling constants $^{1}J(^{195}Pt\,^{1}H)$, $^{1}J(^{195}Pt\,^{31}P)$ and $^{2}J(^{31}P\,^{1}H)$ all decrease from the 4- to 6-coordinated platinum complexes as expected with the corresponding decrease in s orbital character in the bonds. There is also a considerable decrease in $^{1}J(PtH)$ and a smaller one in $^{1}J(PtP)$ from $PtH_2X_2(PEt_3)_2$ to $PtHX_3(PEt_3)_2$. This suggests that there is a decrease in covalency in the Pt-H bond in the same sense, an idea that is supported by the solubility of these complexes: both types of complexes, but particularly the monohydrides, are almost insoluble in non-polar organic solvents.

In the monohydride series $PtHXYZ(PEt_3)_2$, where H is trans to X, $^{1}J(PtH)$ increases in the order X, Y, Z = I, I, I < Br, I, I < Br, Br, I < Br, Br, Br < I, Br, Br < I, Cl, Cl < Br, Cl, Cl. There is therefore a corresponding increase in the s orbital electron density of the Pt-H bond across this series. It has been suggested[19] that halogens do not have a strongly directed labilising influence; both cis and trans influences are significant. The above is then in the order expected from an increase in cis/trans influence of the halogens (and hence decrease in the Pt-H bond energy) in the order Cl < Br < I. In any case, the trends noted above may well be of

value in the determination of structures of soluble complexes.

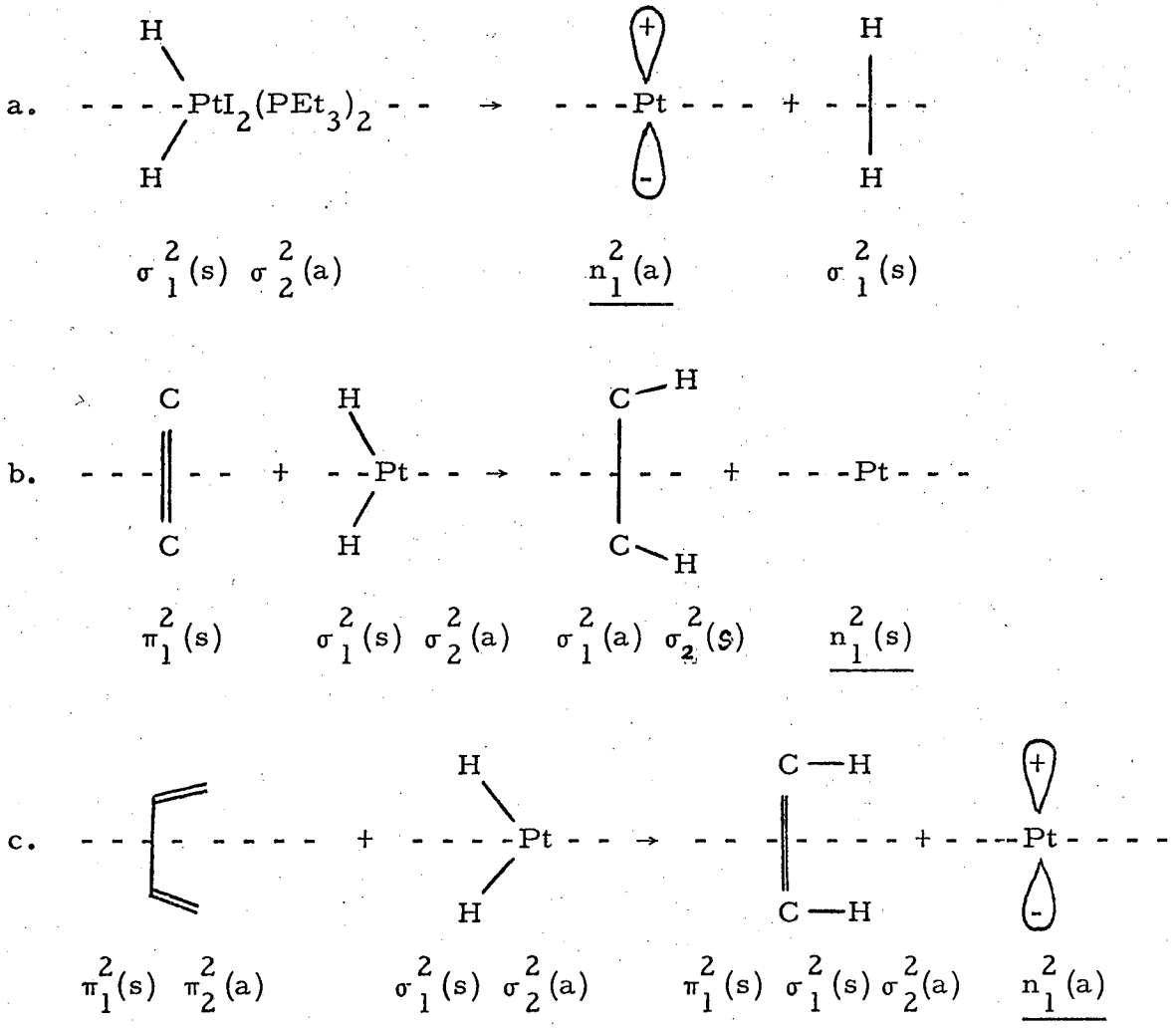
2.6. Attempts to use $PtH_2I_2(PEt_3)_2$ as a hydrogenating agent

As discussed in section 2.2., the cis-dihydride complexes of platinum decompose by loss of hydrogen gas. It was therefore of interest to see whether these complexes could be used as hydrogenating agents. With the hydrogen atoms mutually cis, addition across a double bond might be faciliated.

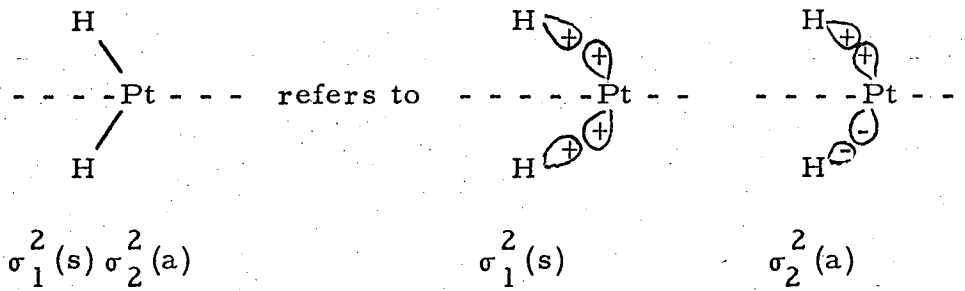
Initially for the hydrogenation reactions, consideration was given to which of the changes in the orbitals involved was symmetry allowed (Woodward-Hoffmann treatment). This is shown diagrammatically in Figure 2.3. For the normal breakdown of the dihydride complex to be a symmetry-allowed process the lone pair of electrons (left in the product complex by the homolytic fission of the two Pt-H bonds) must occupy an orbital which is antisymmetric with respect to the axis shown (Figure 2.3.a.). If the electrons occupied an orbital which was symmetric with respect to this axis then the overall symmetry with respect to the axis would not be maintained during the reaction. Considering the hydrogenation of a mono-ene and a diene in the same way (Figure 2.3 b and c) only the latter gives a product complex in which the lone pair of electrons occupy an orbital which is antisymmetric with respect to the axis. For this reason buta-1,3-diene was used in these reactions.

When equimolar proportions of butadiene and $PtH_2I_2(PEt_3)_2$

Figure 2.3. Symmetry of transitions during oxidation of $PtH_2I_2(PEt_3)_2$



Note: n^2 represents a non-bonding pair of electrons.



were mixed in methylene chloride at room temperature, some hydrogen was evolved and the colour of the solution lightened, indicating the formation of $PtI_2(PEt_3)_2$. The volatile materials from the reaction were separated by gas chromatography. There was no indication of any reduction of butadiene to a mono-ene; instead a small amount of butane was formed. By varying the temperature at which the reaction took place (between 253K and 300K) and the reaction time (between 0.5hr. and several hours) varying amounts of butane were produced, but in no case was the reduction quantitative.

The reaction of butadiene, hydrogen and $PtI_2(PEt_3)_2$ in methylene chloride at room temperature produced very similar quantities of butane. This suggests that, in the above process, the dihydride complex is not acting as a simple hydrogenating agent, but instead as some form of catalyst for the reaction of H_2 with the olefin.

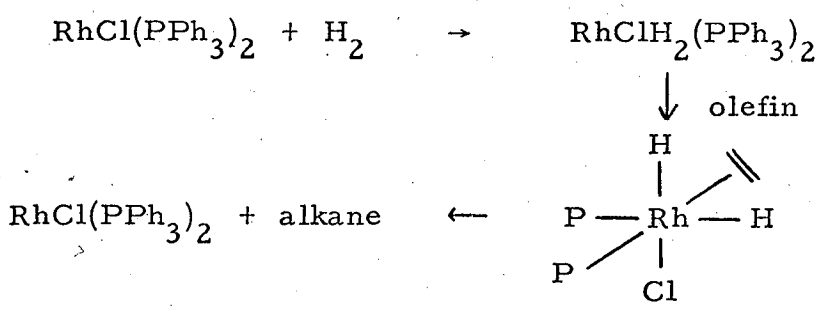
For a complex to be a good homogeneous catalyst it has been suggested that the following conditions must apply,[46]

a) The complex must activate the hydrogen by forming a hydride complex.

b) The complex must also activate the olefin by forming a π-bonded complex. The olefin must be cis to the two hydrogen atoms.

c) The hydrogen atoms must be transferred.

An example of this is given by the homolytic catalytic hydrogenation of an olefin by $RhCl(PPh_3)_2$[46]



The six-coordinated complex $Ir(GeR_3)H_2(CO)(PPh_3)_2$ (R = Me)[48] gave quantitative yields of ethane when reacted with an atmosphere of ethylene at 300K in benzene; incomplete reaction occurred when R = Et. However $IrClH(CO)(PPh_3)_2$ catalysed reduction very slowly even at elevated temperatures[46]; this was explained by the fact that the complex was coordinatively saturated before addition of the olefin. A very similar situation exists with the six-coordinated dihydride complexes of platinum; without losing a ligand cis to the two protons (i.e. a triethylphosphine group) an olefin could not easily become bound to the platinum. Thus, by analogy with the iridium complex, reduction might be expected to be slow at temperatures at which Pt-P (or Pt-I) bonds are stable.

The fact that small amounts of butane were produced on mixing butadiene with hydrogen and $PtI_2(PEt_3)_2$ suggests that there might be some addition of hydrogen to platinum forming a hydride intermediate. An attempt to obtain a Pt-H resonance in the ^1H

n.m.r. spectrum of a mixture of hydrogen and $PtI_2(PEt_3)_2$ was unsuccessful. There was no detectable hydride resonance over the temperature range 183-300K. However a mixture of H_2/D_2, when left over $PtI_2(PEt_3)_2$ in methylene chloride at room temperature for several hours, gave small amounts of HD. Although the reaction mechanism required to produce HD is not fully known, it does suggest that some addition of $H_2(D_2)$ across platinum has taken place.

Hence, from the evidence obtained above, it would appear that cis-trans-$[PtH_2I_2(PEt_3)_2]$ does not act as a hydrogenating agent towards butadiene. Small amounts of catalytic hydrogenation do take place presumably via some form of platinum hydride; the evidence suggests that this hydride may be $PtH_2I_2(PEt_3)_2$.

CHAPTER 3

THE PREPARATION AND SPECTROSCOPIC PROPERTIES OF SOME PLATINUM SILYL AND GERMYL COMPLEXES

3.1. Introduction

In recent years much interest has been centred on the chemistry of transition metals bound to silicon and germanium.[49,50,51] This is probably partly due to compounds of this type appearing as intermediates in the hydrosilation and hydrogermanation of olefins.[52] These compounds are also of interest because of the comparisons which can be made between them and transition metal carbon compounds where only σ bonding is possible in the metal-carbon bond. Most of the work has been concerned with organosilyl and germyl derivatives because of the stability of the products, but recent investigations of the parent hydrides have also been carried out. The work in this chapter deals with the preparation and spectroscopic properties of some silyl and germyl derivatives of platinum. This introduction gives a review of some of the work done in this field.

The first report of the formation of a transition metal-silicon bond was in 1956[53] when $Fe(C_5H_5)SiMe_3(CO)_2$ was prepared by the action of Me_3SiCl on $Na[Fe(h_5\text{-}C_5H_5)(CO)_2]$ over two hours. The compounds, an orange crystalline solid, was thermally stable up to about 473K but decomposed within a day when exposed to atmospheric oxygen. Following this, several other complexes were prepared using the same technique. The reaction of chlorotriphenylsilane with sodium pentacarbonylmanganate in

tetrahydrofuran[54] gave scarlet crystals of $Mn(SiPh_3)(CO)_5$. This compound was air sensitive; the Mn-Si bond was broken by oxidation to give manganese carbonyl, hexaphenyldisiloxane and some triphenylsilanol. The tin and lead analogues of this compound showed greater resistance to oxidation. The first transition metal germyl compounds were also formed in this way in 1962.[55] $Mn(GePh_3)(CO)_5$ and $Fe(C_5H_5)GePh_3(CO)_2$ were prepared by the reaction of the sodium salts of the metals and bromotriphenylgermane; they were stable, pale yellow, crystalline solids.

The complexes described above all contain organo-substituted Group IV B metals. Although they are more stable to oxidation than the parent hydrides, they do have the disadvantage of giving more complex spectra (especially infrared and n.m.r. spectra). MH_3- compounds give infrared spectra with characteristic M-H modes of vibration which are well separated from the modes due to C-H. In the ^1H n.m.r. spectra the M-H proton resonances are chemically shifted from most C-H resonances and are more sensitive to the nature of the transition metal and its substituents. In the organo-compounds there is always at least one more bond between the nearest proton to M and the transition metal.

The first silicon hydride transition metal complex was reported in 1965[56] when silyltetracarbonylcobalt was prepared by treatment of sodium tetracarbonylcobaltate with iodosilane. If

di-iodosilane was used silylene-bis(tetracarbonylcolbalt)[57] could be prepared.

$$SiH_{3-n}I_n + nNa[Co(CO)_4] \xrightarrow{250K} SiH_{3-n}[Co(CO)_4]_n + nNaI$$

$(n = 1, 2)$

The silyl cobalt complexes were volatile liquids which were stable in the vapour phase at room temperature. In common with other silicon hydride compounds, they were air sensitive. The metal-metal bond was cleaved by a variety of protonic reagents including HCl, HF and H_2O to give $CoH(CO)_4$ along with SiH_3Cl, SiH_3F and $(SiH_2O)_x$ respectively.

By reacting iodosilane with sodium pentacarbonylmanganate in ether at 250K, $Mn(SiH_3)(CO)_5$ has been prepared in high yield.[58] The product was a volatile and, when pure, colourless solid which melted at 298K. Although $Mn(SiH_3)(CO)_5$ reacted with air in a similar manner to the cobalt analogue, it was thermally more stable and cleavage of the Mn-Si bond was more difficult. Under normal conditions water reacted only slowly and other reagents (e.g. HX, HgX_2, X = halogen) which would be expected to cleave the Mn-Si bond showed no reaction. In fact, with heating, HCl reacted with liquid $Mn(SiH_3)(CO)_5$ as shown,

$$nHCl + Mn(SiH_3)(CO)_5 \xrightarrow{348K} Mn(SiH_{3-n}Cl_n)(CO)_5 + nH_2$$

$n = 1\text{-}3$

Normally chlorination of SiH_3- by HCl requires a Lewis acid as

catalyst.[59]

Germanium hydride transition metal complexes have been prepared but there are fewer of them. This may be a result of the lower thermal stability of these compounds. The bond energy E(GeH) in GeH_4 is 288 kJ $mole^{-1}$ compared with 320 kJ $mole^{-1}$ for E(SiH) in SiH_4.[60] The first reported complex in this series was bis(pentacarbonylmanganese)germane.[61] This was prepared, not from the sodium salt of the transition metal, but by the action of germane on hydridopentacarbonylmanganese for eight days at room temperature.

$$GeH_4 + MnH(CO)_5 \rightarrow GeH_2[Mn(CO)_5] + H_2$$

Since neither $Mn(GeH_3)(CO)_5$ nor $GeH[Mn(CO)_5]_3$ was observed it was suggested that this reaction did not go via a simple substitution mechanism, but might involve the formation of GeH_2 as an intermediate. $GeH_2[Mn(CO)_5]$ was an air-stable solid which might be a reflection of the greater resistance to oxidation of the GeH bond; E(GeO) in GeO_2 is 355 kJ $mole^{-1}$ in comparison with 469 kJ $mole^{-1}$ for E(SiO) in SiO_2[62]. Germylpentacarbonylmanganese, an air-stable volatile colourless solid, has been prepared by the action of sodium pentacarbonylmanganate on bromogermane.[63]

$$GeH_3Br + Na[Mn(CO)_5] \rightarrow Mn(GeH_3)(CO)_5 + NaBr$$

All the complexes discussed above have an R_3M group

(M = Si, Ge; R = alkyl, aryl, halogen, hydrogen) bound to the transition metal. The metal-metal bond is essentially a σ bond. M, however, has empty d orbitals of the correct symmetry to overlap with filled d orbitals on the transition metal and this introduces the possibility of π bonding. The extent to which this is important in the metal-metal bond is disputed. In some manganese carbonyl complexes it has been claimed that R_3Si and R_3Ge act as good π acceptors as well as σ donors.[64,65,66] Similar properties have been claimed for the metal-metal bond in $Co(MR_3)(CO)_4$[67], but for $Co(SiH_3)(CO)_4$ and $Mn(SiH_3)(CO)_5$ the evidence for $d\pi$-$d\pi$ bonding 'was minimal'[56,58]. From recent studies of the photoelectron spectra of $Mn(MR_3)(CO)_5$ and $Co(MR_3)(CO)_4$[68] it has also been concluded that there is no evidence for $d\pi$-$d\pi$ bonding. A similar conclusion was reached by Hartley for Pt-Si and Pt-Ge complexes in a review of these compounds[51]; the trans influences of silicon and germanium in these complexes could be understood in terms of purely σ bonding in the metal-metal bond.

The first report of a Pt-M (M = Si, Ge) being formed was in 1964 when Glockling[69,70] prepared trans-$[Pt(GePh_3)_2(PEt_3)_2]$ by the reaction,

$$c\text{- or } t\text{-}[PtCl_2(PEt_3)_2] + 2Ph_3GeLi \rightarrow Pt(GePh_3)_2(PEt_3)_2 + 2LiCl$$

The complex was stable to air and moisture but many species

(e.g. MgI_2, LiPh, HCl, H_2) cleaved the Pt-Ge bond.[77] Using a similar reaction some bis-($MePh_2Si$-) and bis(Me_2PhSi-) platinum complexes have been prepared.[71] In contrast to other transition metal-silicon compounds these were stable as solids to air but decomposed when their solutions in tetrahydrofuran or chloroform were exposed to the atmosphere.

Using $(Me_3M)_2Hg$ (M = Si, Ge) instead of the lithium salts Glockling has prepared Me_3M derivatives of platinum.[72,73]

$$(Me_3M)_2Hg + \text{cis-}[PtCl_2(PEt_3)_2] \xrightarrow[\text{reflux}]{C_6H_6} \text{trans-}[PtCl(MMe_3)(PEt_3)_2] + Hg + Me_3MCl.$$

The trimethyl derivatives minimised solubility problems and simplified the spectroscopic properties of the complexes. The trans configuration of the product was confirmed by ^1H n.m.r. spectroscopy. When M = Si the product was rapidly hydrolised by water.

Another method used to prepare platinum silicon complexes was by the action of silicon hydrides on platinum (O) compounds,[74]

$$R_3SiH + Pt(PPh_3)_4 \rightarrow \text{cis-}[PtH(SiR_3)(PPh_3)_2] + 2PPh_3$$

$$2R_3SiH + Pt(PPh_3)_4 \rightarrow \text{cis-}[Pt(SiR_3)_2(PPh_3)_2] + 2PPh_3 + H_2$$

Which reaction pathway was followed depended on the nature of the group R and the reaction conditions [R_3Si was Cl_3Si-, Ph_2HSi, $(m\text{-}F.C_6H_4)_3Si$-, $(m\text{-}CF_3.C_6H_4)_3Si$- and $(p\text{-}CF_3.C_6H_4)_3Si$-]. A

similar reaction was observed for $Pt(diphos)_2$ (diphos = $Ph_2P(CH_2)_2PPh_2$). When $Pt(SiHPh_2)_2$ (diphos) was treated with one molar proportion of bromine the final product still contained Pt-Si bonds; $Pt(SiBrPh_2)_2$(diphos) was formed. Two molar proportions of bromine did, however, cleave the Pt-Si bond.

A third method used to form silicon or germanium platinum bonds is illustrated in the following reaction,[71,75]

$$R_3MH + \text{trans-}[PtClH(PEt_3)_2] \rightarrow \text{trans-}[PtCl(MR_3)(PEt_3)_2] + H_2.$$

The reaction appeared to be assisted by electron-withdrawing groups on M. By an analogous reaction, Bentham[76] has prepared a series of stable silyl and germyl hydride complexes of platinum.

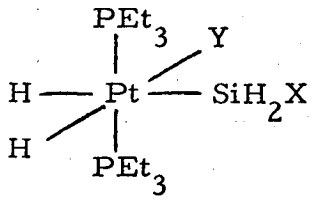
$$MH_3X + \text{trans-}[PtHY(PEt_3)_2] \rightarrow \text{trans-}[Pt(MH_2X)Y(PEt_3)_2] + H_2$$

(X, Y = halogen)
(X = H)

When M = Si, X, Y = Cl, treatment of the complex with an excess of HCl gave the ultimate product $PtCl(SiCl_3)(PEt_3)_2$; only when the solid was treated with liquid HCl was the Pt-Si bond cleaved.

The last two reactions were thought to proceed via the same mechanism. It was postulated that the first step was oxidative addition of the R_3M-H bond across Pt to give a six-coordinated platinum (IV) complex at an intermediate which then eliminated two ligands to form the product.

$$MH_3X + PtHY(PEt_3)_2 \xrightarrow{slow}$$

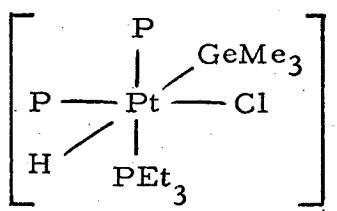


$$\xrightarrow{fast} Pt(SiH_2X)Y(PEt_3)_2 + H_2$$

This intermediate was not detected in either reaction but when SiH_3X (X = Cl, I) was mixed with trans-$[PtI_2(PEt_3)_2]$ at 250K[76], cis-trans-$[PtHI_2(SiH_2X)(PEt_3)_2]$ was isolated. Six-coordinated complexes have been postulated as intermediates in several reactions involving silicon and germanium platinum complexes. The cleavage of Pt-M (M = Group IV B metal) bonds by reactants such as hydrogen halides, halogens and alkyl halides are all believed to proceed by cis addition to the Pt-M complex to give a labile Pt(IV) complex as an intermediate which then decomposes by Pt-M bond cleavage to yield the final product. An example of this was the cleavage of the Pt-Ge bond in

$[Pt(GeMe_3).PEt_3.(diphos)]Cl$ by dry HCl[75]

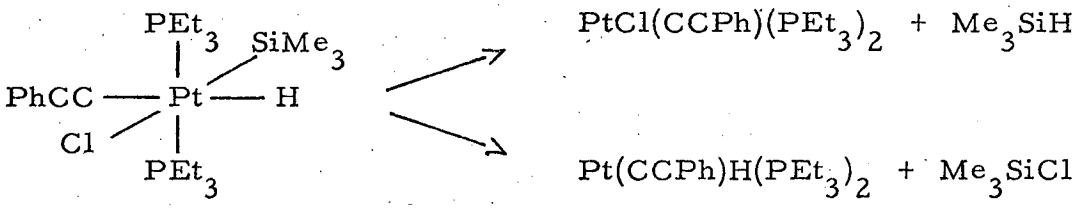
$$[Pt(GeMe_3)PEt_3(diphos)]Cl + HCl \xrightarrow{C_6H_6}$$



or an isomer

$$\xrightarrow{CH_3OH} [PtH(PEt_3)(diphos.)]Cl + Me_3GeCl.$$

The six-coordinated platinum complex was isolated as a white precipitate from benzene; on redissolving in methanol Me_3GeCl was liberated leaving the four-coordinated ionic complex. Another reaction, in which the observed products were explained by two modes of elimination from a six-coordinated platinum complex was that of phenyl acetylene with trans-$[PtCl(SiMe_3)(PEt_3)_2]$.[73]



Several minor products were also detected. Although many platinum (IV) complexes are thought to exist as labile intermediates in the reactions of silyl and germyl platinum complexes, as yet few have been isolated and characterised.

3.2. General Reactions

In this Chapter the reactions of some substituted silyl and germyl hydrides with four-coordinated platinum complexes are described and the spectroscopic properties of the products considered. The reactions considered were

(a) those of SiH_3X (X = CN, C_5H_5, CCH, $CCCF_3$), $GeH_3C_5H_5$ and Si_3H_8 with trans-$[PtHY(PEt_3)_2]$ and trans-$[PtY_2(PEt_3)_2]$ (Y = halogen), and

(b) those of silyl halides with trans-$[Pt(CCX)_2(PEt_3)_2]$ (X = H, Ph,

CF_3) and trans-$[Pt(CH_3)I(PEt_3)_2]$. There were two objectives of this study. First it was carried out to see whether different types of reaction products might be formed by substituting on the Group IV atom groups which might also attack the platinum complexes. Second, it has been suggested[78] that the rate determining step in the preparative reaction for platinum-silicon complexes is electrophilic attack by silicon on platinum. It was therefore hoped that, by substituting on platinum ligands of differing electronic properties, the rate of this reaction could be varied.

3.3. Reactions of Silyl and Germyl Compounds bound to Unsaturated Substituents

Despite the large number of σ and π bonded acetylene and cyclopentadiene complexes of platinum known,[79,80,81] there were no indications of any of the unsaturated groups bound to M interacting with platinum. In all the reactions considered the normal pathway of oxidative addition of M-H (M= Si, Ge) across Pt followed by elimination of two ligands was followed.[76]

SiH_3X ($X = C_5H_5$, CCH, $CCCF_3$) reacted smoothly with equimolar amounts of $PtHY(PEt_3)_2$ (Y = Cl, I) at room temperature in a suitable solvent (C_6H_6, CH_2Cl_2, CCl_3F). Hydrogen was evolved and the silyl-platinum complex formed.

$$SiH_3X + PtHY(PEt_3)_2 \rightarrow Pt(SiH_2X)Y(PEt_3)_2 + H_2$$

The rate of the reaction varied considerably with X. SiH_3CCCF_3

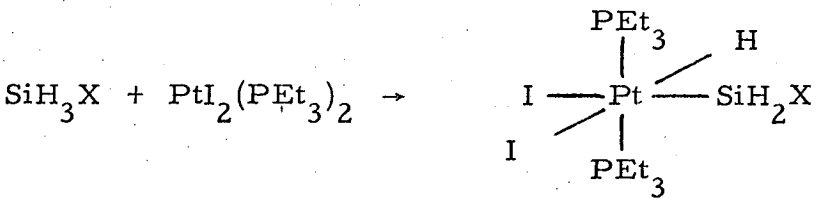
reacted rapidly, effervescence being complete within 0.25 hr. The reactions of SiH_3CCH and $SiH_3C_5H_5$ were slower; for Y = Cl the former only gave complete reaction after 30 hrs at 300K while for the latter 100% reaction was not attained. All the substituents contain multiple bonds and so are relatively electron rich. If the rate determining step in the above reaction is the electrophilic attack of Si-H on Pt then, with these substituents on silicon, the reaction rate might be expected to be reduced. This is observed for SiH_3CCH and $SiH_3C_5H_5$ although for the latter steric effects must also be important. For SiH_3CCCF_3 the electrons are withdrawn by $-CF_3$ from the carbon atom bound to the silicon. This leads to an increase in the reaction rate.

By evaporation of the solvent at 250K, some of the products were isolated as white or pale yellow crystalline solids. They were stable under vacuum for several days but decomposed readily when exposed to the atmosphere. The solids were characterised by their infrared spectra and C, H analyses (Chapter 8). All the complexes were characterised in solution by their n.m.r. spectra and this is discussed in section 3.4. $GeH_3C_5H_5$ reacted in the same way as $SiH_3C_5H_5$ but the reaction was faster. Unlike the complexes $Pt(GeH_2X)Y(PEt_3)_2$ (X, Y = halogen), which decompose on removal of the solvent,[76] $Pt(GeH_2C_5H_5)I(PEt_3)_2$ was isolated as a pale yellow solid by evaporation of the solvent at 250K. The product was of similar in stability to the silyl analogue; the infrared

parameters are included in Chapter 8.

The action of SiH_3CN on $PtHX(PEt_3)_2$ (X = halogen), differed for those above in that very rapid halogen/cyanide exchange occurred first giving SiH_3X and $Pt(CN)H(PEt_3)_2$; these compounds then reacted in the normal manner to give the complex $Pt(CN)SiH_2X(PEt_3)_2$. Values for Pt-Y (Y = halogen, cyanide) bond energies are not well characterised but an indication of their relative stabilities can be obtained from thermodynamic data. $\Delta G^o f$ $[Pt(CN)_4^{-2}$ aq.] is approximately 707 kJ $mole^{-1}$ compared with 129, 288 and 380 kJ $mole^{-1}$ for the tetraiodide, tetrabromide and tetrachloride respectively.[82] The ability of the cyano group to strengthen the metal-ligand bond by π bonding may account for this in part. Although the Si-C bond energy in SiH_3CN has not been determined this bond is longer[83] than the Si-C bond in SiH_3CCH (see Chapter 6); this suggests that it may be a weaker bond and would therefore help to push the equilibrium over towards Pt-CN and Si-halogen.

The reactions of SiH_3X (X = CCH, $CCCF_3$) with trans-$[PtI_2(PEt_3)_2]$ were also studied. When equimolar proportions of these compounds were mixed at 273K in benzene solvent a colour change indicated that a chemical change had taken place. No hydrogen was evolved. Oxidative addition of Si-H across Pt had formed a six-coordinated complex; this was analogous to complexes already observed.[76]



The same adduct was formed by addition of equimolar proportions of HI to a solution of $PtI(SiH_2CCX)(PEt_3)_2$ (X = H, CF_3) in benzene. At temperatures below 273K these complexes were stable, but on warming slow decomposition took place. Careful evaporation of the solvents at 250K left pale yellow solids which, for X = $CCCF_3$, showed no signs of decomposition. When X = CCH, slow decomposition of the solid left a deeply coloured oil. Both solids were characterised by infrared spectroscopy and C, H analysis, (Chapter 8.) They were also studied by ^1H n.m.r. spectroscopy and this is discussed in the following section.

3.4. ^1H n.m.r. Spectra

The ^1H n.m.r. spectra of the M<u>H</u> protons in all the products and the Pt<u>H</u> protons in the six-coordinated complexes have been studied. For both types of protons, the resonances are split into a 1:4:1 triplet due to coupling with ^{195}Pt (33.7 % abundance) and then each is further split into a 1:2:1 triplet from coupling with the two equivalent ^{31}P nuclei. These parameters, along with chemical shifts and coupling constants associated with nuclei in the unsaturated groups, are recorded in Tables 3.1 - 3.4. The

protons in the Et_3P groups give rise to complex resonances at approximately 8T (CH_2) and 9T (CH_3). The $-CH_3$ and $-CH_2-$ resonances are split into triplets and quartets respectively from coupling with each other. These are then further split into triplets by the two ^{31}P nuclei ; this is due to virtual coupling which arises because of strong ^{31}P - ^{31}P coupling.[84] The resonances are characteristic of mutually trans Et_3P groups in square planar[85] or octahedral platinum complexes. Heteronuclear double resonance was used to confirm the assignments of coupling constants and also to determine their signs and to measure ^1J(Pt-P), $\delta(^{195}Pt)$ and $\delta(^{31}P)$.

(i) Reactions of SiH_3CCX (X = H, CF_3) with $PtHY(PEt_3)_2$ and $PtY_2(PEt_3)_2$ (Y = Cl, I) *

The n.m.r. parameters for the products are given in Tables 3.1. and 3.2. In the spectrum of $PtCl(SiH_2CCH)(PEt_3)_2$ the start of decomposition of the product was associated with broadening of the ^1H resonances and collapse of the coupling HCCSiH was observed in the SiH resonance followed by collapse of $^{④??}J$(HSiPtP). The HCC- resonance remained a sharp triplet [due to ^4J(HCCSiH)]. These observations can be understood if decomposition

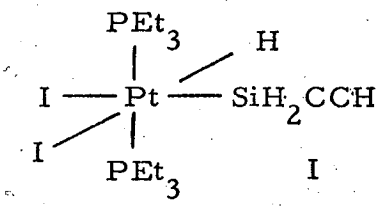
* For X = H, Y = Cl a preliminary study of the ^1H n.m.r. was carried out as a final year project. This work was repeated.

liberates Et_3P which induces exchange with coordinated Et_3P that is fast on the n.m.r. timescale; then couplings to ^{31}P would be expected to collapse but couplings within the $HCCSiH_2Pt$ fragment would not be affected. In the analogous complex $PtI(SiH_2CCH)(PEt_3)_2$ this collapse was not observed; here the doublet splitting due to $^4J(HSiCCH)$ was not resolved in the ^{195}Pt satellites of the main Si<u>H</u> resonance, but effects of this kind in the spectra of other Pt-I complexes are believed to be due to relaxation of the ^{195}Pt spin due to scalar coupling to the ^{127}I nucleus.[86] It was not possible to confirm that this explanation was correct by observing the ^{195}Pt satellites of the <u>H</u>CC resonance which were obscured by peaks due to the Et_3P groups.

Reaction of SiH_3CCH with a 2:1 excess of $PtClH(PEt_3)_2$ under the same conditions gave the same products with the same n.m.r. spectrum; there was no evidence of weak interaction or of reaction between the acetylene group and the platinum complexes. With a 2:1 excess of SiH_3CCH the same initial product was also formed, but after a few days at room temperature the benzene solution separated into two layers. The oily lower layer was strongly coloured, and the upper layer very pale; both showed only weak and broad n.m.r. signals. A similar effect was observed in the reactions between other platinum complexes and an excess of silane or silyl halide.[76]

In the six-coordinated mono-hydride complex,

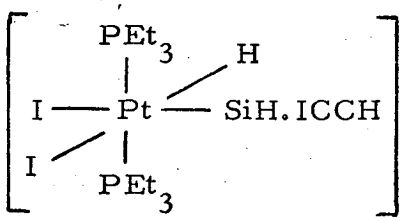
$PtHI_2(SiH_2CCH)(PEt_3)_2$(I) resonances due to Pt<u>H</u> and Si<u>H</u> were observed at 258K. The SiH_2CCH and H ligands are believed to be mutually cis because ^3J(<u>H</u>PtSi<u>H</u>) was not observed; in related germyl complexes ^3J(trans <u>H</u>PtGe<u>H</u>) is about 10 Hz.[87] At 273K the proton resonances were broad presumably because of exchange between this adduct and trans-$[PtI(SiH_2CCH)(PEt_3)_2]$. If a solution of the adduct in benzene was kept at room temperature, its n.m.r. signal slowly disappeared and new peaks developed which were assigned to trans-$[PtI(SiHICCH)(PEt_3)_2]$ (II) and to $SiH_2I.CCH$ (Si<u>H</u> doublet, 5.37τ, ^4J(HH) = 0.8 Hz). This solution was stable for several days. On prolonged standing a weak peak (doublet, 4.16τ, ^4J = 1.7 Hz) appeared, perhaps due to $SiHI_2.CCH$. These observations can be explained by the following reaction scheme,



$$\rightarrow \quad SiH_2I.CCH \; + \; PtHI(PEt_3)_2$$

$$PtHI(PEt_3)_2 \; + \; SiH_2I.CCH \quad \rightarrow \quad PtI(SiHICCH)(PEt_3)_2(II) \; + \; H_2$$

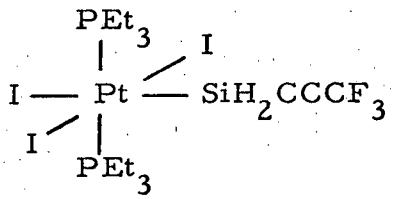
Also $PtI_2(PEt_3)_2$ + $SiH_2I.CCH$ →



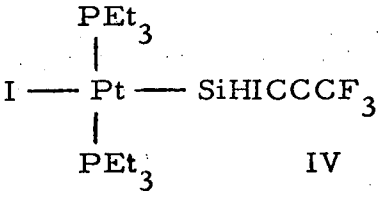
→

$$PtHI(PEt_3)_2 \; + \; SiHI_2.CCH$$

The complexes prepared from SiH_3CCCF_3 gave very similar n.m.r. parameters; the effect of the electron-withdrawing CF_3 group was very slight. The six-coordinated adduct III decomposed slowly to give a compound identified by its n.m.r. spectrum as trans-$[PtI(SiHI.CCCF_3)(PEt_3)_2]$ IV



III



IV

Exchange of HI between III and $PtI(SiH_2CCCF_3)(PEt_3)_2$ was faster than for the analogous derivative of SiH_3CCH; sharp resonances were only observed at 238K and couplings due to ^{19}F were not observed.

(ii) Reactions of $MH_3C_5H_5$ (M = Si, Ge) with $PtHX(PEt_3)_2$ (X = Cl, I).

The compounds $^1h\text{-}C_5H_5MH_3$ (M = Si, Ge), as with many other σ bonded cyclopentadienyl compounds, show temperature dependent fluxional behaviour;[88,89] this migration is thought to go via a 1,2 metalotropic shift. At low temperatures the ^1H n.m.r. spectrum of $^1h\text{-}C_5H_5MH_3$ (M = Si, Ge) is an $AA^1BB^1MX_3$ system which simplifies to an AX_3 system on warming the sample. The coalescence temperature varies widely over the range of compounds which have been studied and within the Group IV cyclopentadienyl

Table 3.1. Chemical Shifts in Acetylenosilyl Complexes of Platinum (ppm)

	τ(SiH)	τ(CH^1)	τ(PtH)	δ(Pt)(a)	δ(P)(b)	ϕ(F)(c)
t-[$PtCl(SiH_2CCH^1)(PEt_3)_2$]	6.47	7.81	-	-187	+16.7	-
t-[$PtCl(SiH_2CCCF_3)(PEt_3)_2$]	6.88	-	-	-173	+16.1	51.3
t-[$PtI(SiH_2CCH^1)(PEt_3)_2$]	6.40	n.o.	-	n.o.	n.o.	-
c-t-[$PtHI_2(SiH_2CCH^1)(PEt_3)_2$]	6.00	n.o.	23.46	-369	-14.0	-
c-t-[$PtHI_2(SiH_2CCCF_3)(PEt_3)_2$]	6.27	-	23.26	-427	-14.5	n.o.
t-[$PtI(SiHICCH^1)(PEt_3)_2$]	5.72	n.o.	-	-249	+ 7.2	-
t-[$PtI(SiHICCCF_3)(PEt_3)_2$]	5.86	-	-	n.o.	n.o.	n.o.

n.o. = not observed

(a) δ(Pt) is relative to 0.5 M solution of trans $H(Et_3P)_2PtCl$ in CH_2Cl_2 (external standard)

(b) δ(P) " " " 85% H_3PO_4 (" ")

(c) ϕ(F) " " " CCl_3F (internal ")

τ values were measured relative to Me_4Si internal standard.

Table 3.2. Coupling Constants (Hz)

	^1J(PtP)	^1J(PtH)	^2J(PtH)	^2J(PH)	^3J(PH)	^4J(PtH)	^4J(HH)	^5J(PtF)	^5J(FF
$PtCl(SiH_2CCH)(PEt_3)_2]$	+2480	-	+43.5	-	+8.8	-15.4	-1.4	-	-
$PtCl(SiH_2CCCF_3)(PEt_3)_2]$	+2420	-	+45.0	-	+8.8	-	-	+23.7	2.2
$PtI(SiH_2CCH)(PEt_3)_2]$	-	-	+51.4	-	+9.3	n.o.	-1.4	-	-
$-[PtHI_2(SiH_2CCH)(PEt_3)_2]$	+1690	+1226	+19.0(a)	-5.5	+8.6	n.o.	-1.3	-	-
$-[PtHI_2(SiH_2CCCF_3)(PEt_3)_2]$	n.o.	+1113	n.o.(b)	-5.8	+7.7	-	-	-	n.o.
$PtI(SiHICCH)(PEt_3)_2]$	+2380	-	+131.4	-	+12.7	n.o.	n.o.	-	-
$PtI(SiHICCCF_3)(PEt_3)_2]$	-	-	+128.5	-	+12.3	-	-	-	2.3

PtH) and ^1J(PtP) assumed +ve.

Relative magnitudes of ^2J(PtH) and ^3J(PH) allow only the outer lines of the Pt satellites to be observed.

Pt satellites are under broadened ^{31}P triplet; hence ^2J(PtH) 2 x ^3J(PH).

). = not observed.

compounds the coalescence temperature decreases from carbon to tin.

C_5H_5 substituent	Approximate coalescence temperature (K)
Me_3Si-	343
H_3Si-	303
Cl_3Si-	323
F_3Si-	308
Me_3Ge-	293
H_3Ge-	298
Me_3Sn-	148
F_2P-	323

On complexing ^{1}h-$C_5H_5MH_3$ to platinum the rate of fluxionation, rather surprisingly, increased. Although the reason for this is not understood, it may be that, on formation of the slightly sterically crowded product, the $C_5H_5MH_3$ fragment is distorted towards the transition state configuration required for migration; this would effectively lower the activation energy. Another possible explanation is that the transition state is stabilised by interaction with the d orbitals on platinum. Changing the halogen bound to platinum from chloride to iodide had no noticeable effect on the rate of migration, but for both M = Si and Ge it did have the effect of increasing the separation of the AA^1 and BB^1 components of the subspectrum by about 3 Hz. In the absence of any direct platinum-

ring interaction this effect must have been transmitted over five or six bonds. The changes in the ^{1}H n.m.r. spectrum with temperature for $Pt(GeH_3C_5H_5)I(PEt_3)_2$ in CCl_3F solvent are shown in Figure 3.1. At low temperatures the high and low frequency ^{195}Pt satellites of the GeH resonance are obscured by the resonances of the proton on the saturated ring carbon atom and the EtP group respectively. Because of the low temperature required to obtain the 'frozen' form of the germyl complexes, viscosity of the solution and insolubility of the products broadened the resonances enough to obscure the coupling $^{3}J(HCGeH)$; this problem did not arise with the silyl complexes because of the slower rate of fluxionation and the coupling was observed and confirmed by homonuclear double resonance (Figure 3.2.). The n.m.r. parameters are gathered in Table 3.3.

The stability of the chloro-complexes was lower than that of the iodo complexes; the former decomposed, with associated broadening of the ^{1}H n.m.r. spectrum, after about 1 - 2 hrs. at room temperature giving separation into two layers.

(iii) Reactions of MH_3X (X = H, Cl) with $PtH(CN)(PEt_3)_2$*

Because of rapid halogen/cyanide exchange, only the reactions of MH_3X (X = H, halogen) with cyano-platinum complexes

* Preliminary studies of the ^{1}H n.m.r. spectra of some of the silyl complexes was carried out as part of a vacation project. This work has been repeated.

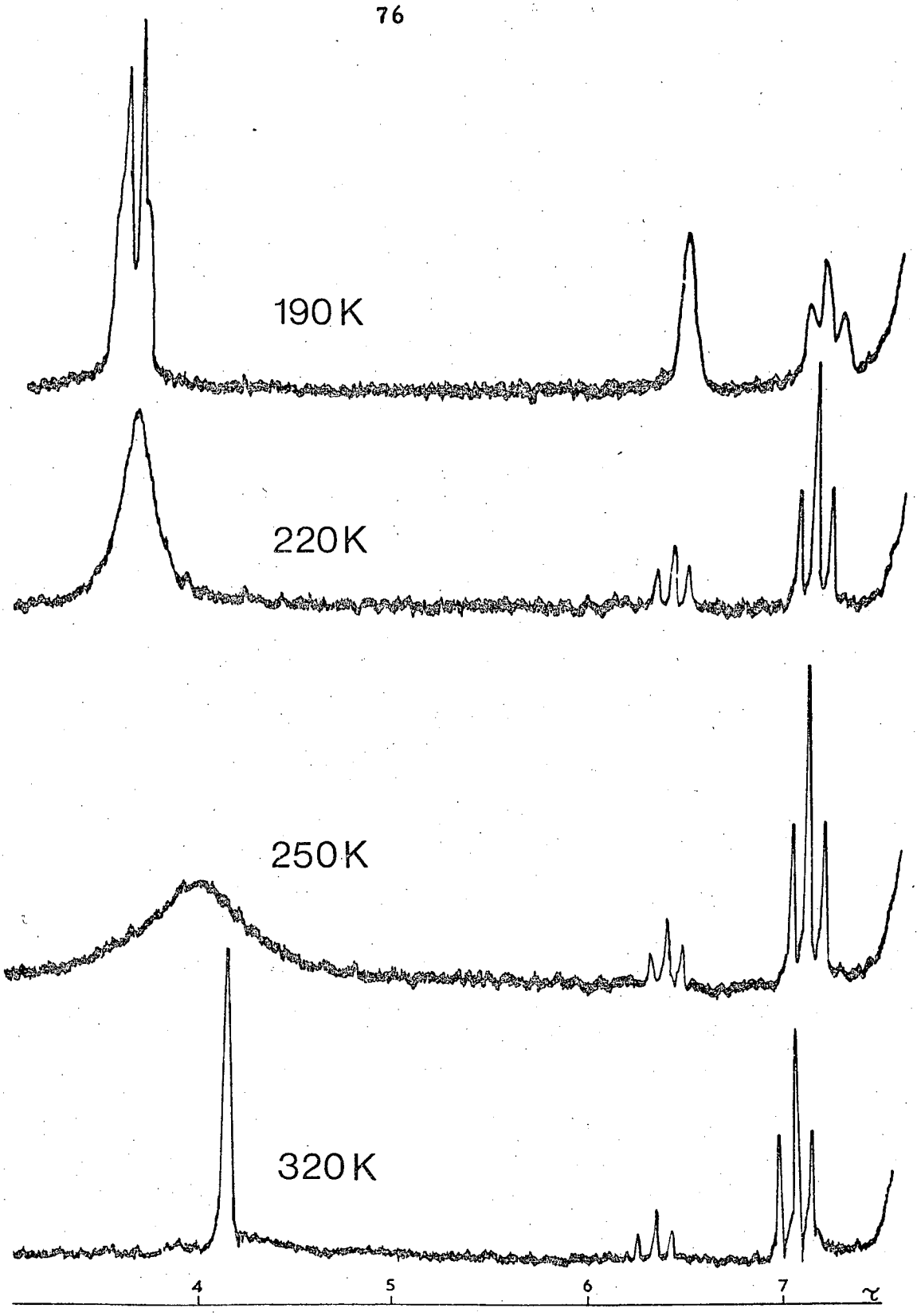


Fig. 3. 1. Variation in ^{1}H n.m.r. spectrum of t-$[Pt(GeH_2C_5H_5)I(PEt_3)_2]$ with temperature.

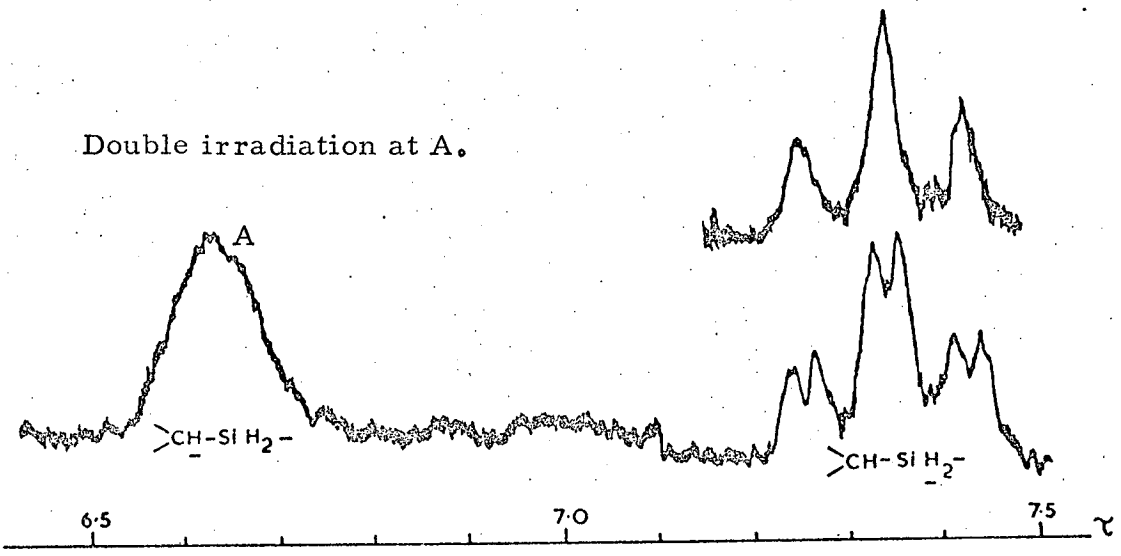


Fig. 3.2. Homonuclear double irradiation of the $C\underline{H}$-SiH_2- proton in t-$[PtCl(SiH_2C_5H_5)(PEt_3)_2]$.

were studied. The main feature of the ^{1}H n.m.r. spectra of all the complexes $Pt(CN)(MH_2X)(PEt_3)_2$ (except $MH_2X = GeH_3$) was that the coupling $^{3}J(\underline{P}PtM\underline{H})$ was not observed at room temperature; the Et_3P proton resonances had also simplified to the triplet and quartet pattern expected from a $CH_3.CH_2-$ group. This can be understood if there is Et_3P exchange similar to that observed for $PtCl(SiH_2CCH)(PEt_3)_2$; this however does not explain why the $CH_3.CH_2-$ resonances are not split into doublets by the ^{31}P to which they are bound. If the signs of J(PH) change between free and complexed Et_3P and under conditions of rapid exchange the value of the coupling constants average to approximately zero, then these couplings would not be observed. Other reports on the values of $^{2}J(PH)$ and $^{3}J(PH)$ in free and complexed phosphines suggest that the coupling constants are small (< 20 Hz) and may take either sign.[15,90] The complex $Pt(CN)GeH_3(PEt_3)_2$ initially showed coupling with ^{31}P but after one hour at room temperature this disappeared. The weakening of the Pt-P bond must be related to the influences of the cis ligands. The cyano ligand is known to have a strong cis effect[22] but, since coupling with ^{31}P is observed in the proton spectrum of trans-$[Pt(CN)H(PEt_3)_2]$, this alone cannot be strong enough to cause Et_3P exchange. It must be due to the combined cis effects of the CN and MH_2X ligands. If $^{1}J(Pt-P)$ is used as a measure of the degree of Pt-P bond weakening (cf. Chapter 1) then from the following table (Et_3P ligands omitted)

Table 3.3. n.m.r. parameters for $Pt(MH_2C_5H_5)X(PEt_3)_2$

	M=Si, X=Cl	M=Ge, X=Cl	M=Si, X=I	M=Ge, X=I
$\tau(M\underline{H})^a$ (ppm)	7.22	7.38	7.02	7.07
$\tau(C_5\underline{H}_5)^b$ (ppm)	4.15[c]	4.19	4.17	4.16
$\tau(-C\underline{H})^d$ (ppm)	6.64	6.49	6.63	6.48
$\tau(\underline{\quad}\!\!\bigcirc\!\!\underline{\quad})^d$ (ppm)	3.57	3.58	3.57	3.62
$\delta(Pt)^{a,e}$ (ppm)	-175	-101	-345	-386
$\delta(P)^{a,f}$ (ppm)	+ 16.8	+ 13.3	+ 10.7	+ 6.6
$^1J(PtP)^a$ (Hz)	+ 2580 (30)	+ 2495 (20)	+ 2280 (20)	+ 2480 (20)
$^2J(PtH)^a$ (Hz)	+ 72.6	+ 140	+ 78.4	+ 144.5
$^3J(PH)^a$ (Hz)	+ 8.7	+ 8.4	+ 9.2	+ 8.2
$^3J(\underline{H}MC\underline{H})^d$ (Hz)	2.8	n.o.	2.9	n.o.

n.o. = not observed

a. measurements made at 300K

b. " " " 323K

c. peaks not sharp at 320K

d. measurements made at 193K

e. $\delta(Pt)$ to high frequency of 0.5M trans-$[PtClH(PEt_3)_2]$ in CH_2Cl_2 (external standard)

f. $\delta(P)$ " " " " 85% H_3PO_4. (external standard)

Compounds	^1J(Pt-P) Hz
Cl - Pt - H	2730 (15)
NC - Pt - H	2546 (25)
NC - Pt - GeH_3	2349 (12)
NC - Pt - SiH_3	2328 (10)
NC - Pt - SiH_2CN	2195 (20)
NC - Pt - GeH_2Cl	2100 (80)

it can be seen that this correlates well with the observance or non-observance of Et_3P exchange; complexes with ^1J(Pt-P) of less than approximately 2400 Hz exhibit Et_3P exchange. ^{31}P coupling might have been expected initially for the complex $Pt(CN)SiH_3(PEt_3)_2$ but, since the reactants had to be left at room temperature for 24 hours before the product resonance was strong enough to observe (cf. 10 min. for germyl analogue), it is likely that these would be phosphine exchange by this time. The exchange of phosphines could be stopped by lowering the temperature to 220K; examples of the 'exchanging' and 'non-exchanging' spectra are given in Figure 3.3. and the n.m.r. parameters are listed in Table 3.4.

3.5. Reaction of Si_3H_8 with $PtHI(PEt_3)_2$

Trisilane reacts with $PtHI(PEt_3)_2$ via an addition-elimination mechanism analogous to that described above; however in this case there are two different silicon atoms at which this attack could

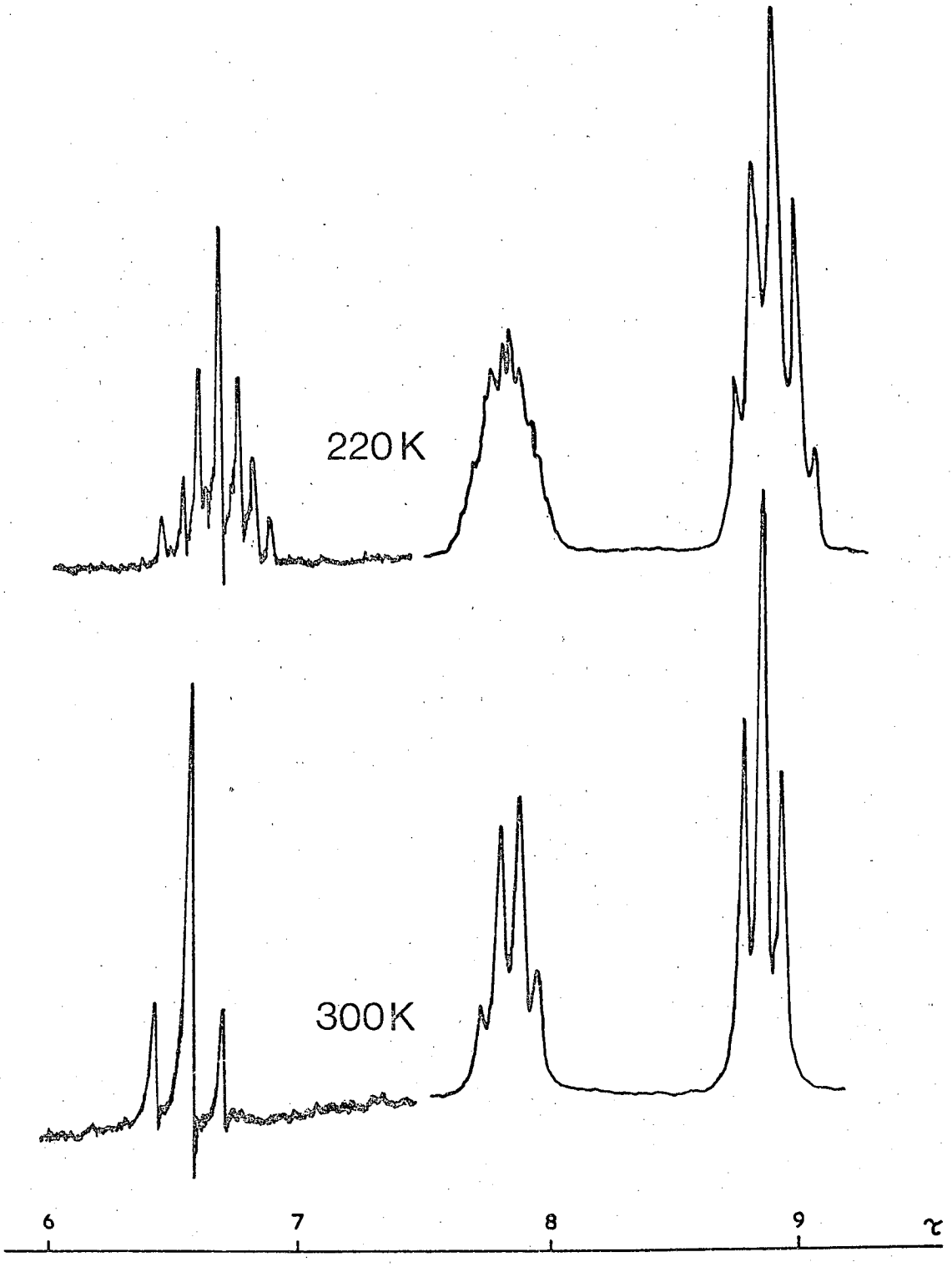


Fig. 3.3. Variation in ^{1}H n.m.r. spectrum of t-$[Pt(CN)SiH_2CN(PEt_3)_2]$ with temperature.

occur. With equimolar proportions of Si_3H_8 and $PtHI(PEt_3)_2$ in benzene/tetramethylsilane there was rapid evolution of hydrogen at 273K and a yellow solution resulted. This gave a complex ^1H n.m.r. spectrum (Figure 3.4a.) which could not be solved completely. Of the two 1:1 products expected (Pt-$SiH_2SiH_2SiH_3$(I) and Pt-$SiH(SiH_3)_2$(II)) resonances have been assigned to the SiH_3 protons of both and these parameters are given below.

	τ(ppm)	^3J(HH) Hz	^4J(PtH) Hz
$PtI[SiH(SiH_3)_2](PEt_3)_2$	6.29	3.9	36.4
$PtI(SiH_2SiH_2SiH_3)(PEt_3)_2$	6.48	~3	n.o.

From the peak heights the ratio of II:I was approximately 2:1 compared with 3:1 for the theoretical random distribution of products. Using a 3:1 excess of $PtHI(PEt_3)_2$ a spectrum similar to Figure 3.4a was obtained initially but, when left at 273K, effervescence continued and a deep red solution resulted in a few hours. The ^1H spectrum simplified during this further reaction (Figure 3.4.b) suggesting that a more symmetrical product(s) had been formed. However, even with homonuclear double resonance, no further information could be obtained from the spectrum. The volume of hydrogen evolved in this reaction was measured and 0.4 m.moles of hydrogen was obtained from 0.14 m.moles of Si_3H_8. This suggests that there must have been a considerable amount of di-platinum substitution on Si_3H_8 and a significant amount of tri-

Table 3.4. N.M.R. Parameters for $Pt(CN)X(PEt_3)_2$

X	τ (ppm)	δ(Pt) ppm	δ(P) ppm	$^1J(PtP)$ Hz	$^2J(PtH)$ Hz	$^3J(PH)$ Hz
SiH_3 [a]	7.07	-296	-11.0	+ 2328 (10)	+ 11.8	+ 6.1
SiH_2Cl [b]	4.96	n.o.	n.o.	n.o.	+ 73.5	n.o.
SiH_2Br [b]	5.52	n.o.	n.o.	n.o.	+ 77.7	n.o.
SiH_2CN [c]	6.68	-309	- 9.7	+ 2195 (20)	+ 27.8	+ 7.9
GeH_3 [b]	6.87	-248	- 9.9	+ 2349 (12)	+ 46.5	+ 5.5
GeH_2Cl [b]	4.52	-236	n.o.	+ 2100 (80)	+ 140.2	n.o.

n.o. = not observed

a. measurement made in CH_2Cl_2 at 200K. τ(SiH) = 6.93 at 300K in CH_2Cl_2 and 6.48 in C_6H_6 at 300K.

b. " " " C_6H_6 " 300K.

c. " " " CH_2Cl_2 " 233K. τ(SiH) = 6.56 at 300K in CH_2Cl_2.

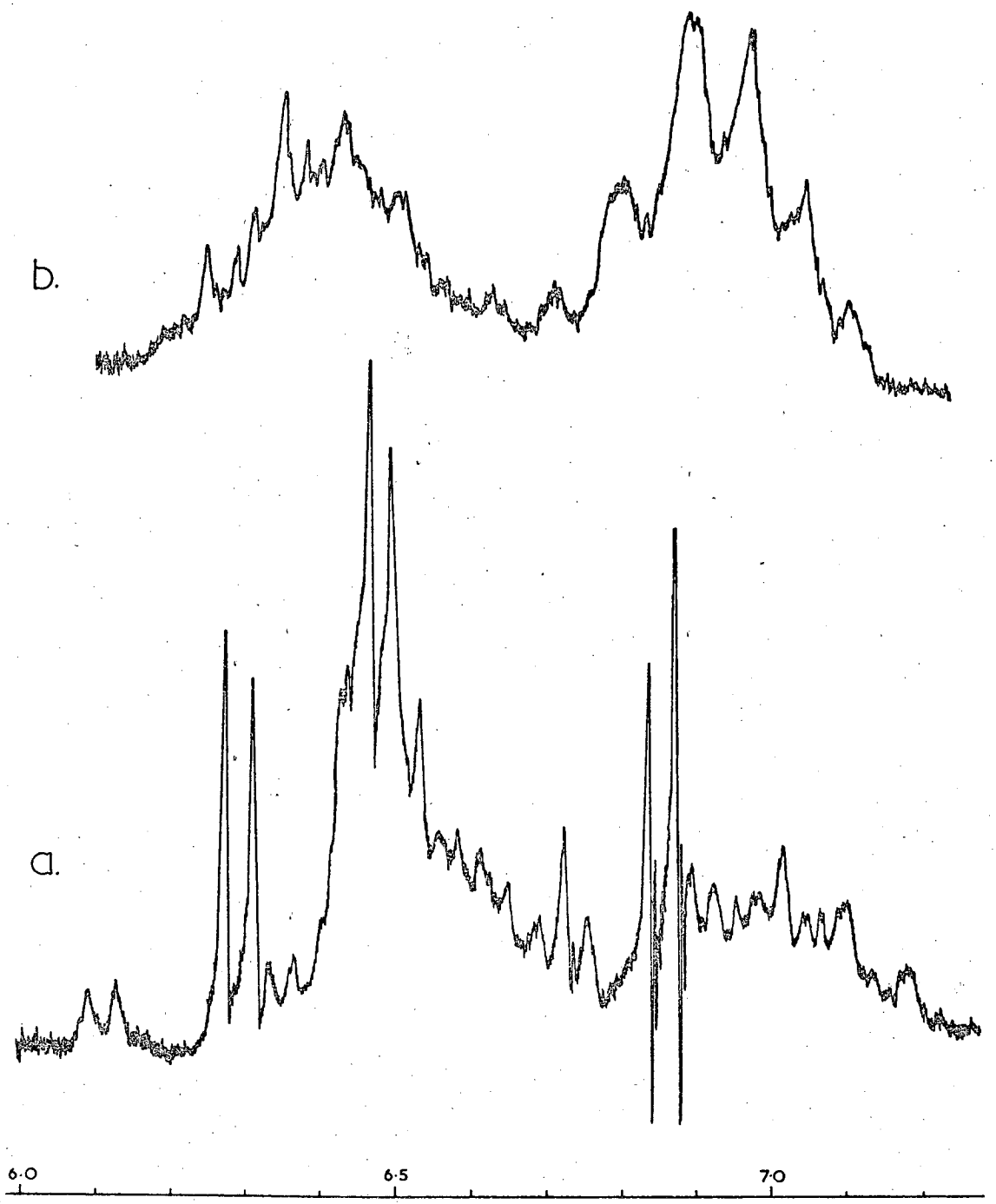


Fig. 3.4. ^{1}H n.m.r. spectra of (a) 1:1 and (b) 1:2 mixtures of Si_3H_8 and t-$[PtI_2(PEt_3)_2]$ after several hours at 273K.

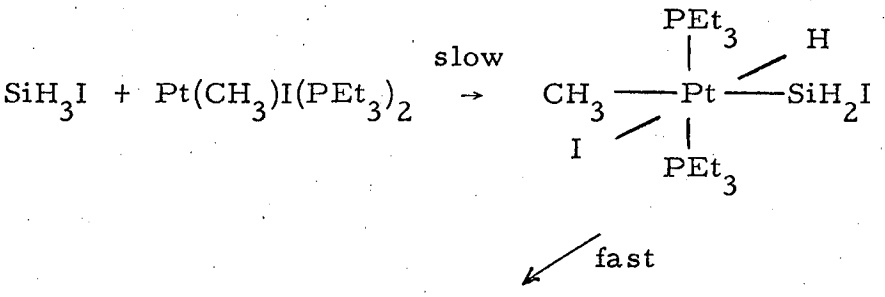
platinum substitution.

3.6. Reactions of silyl halides with trans-$[Pt(CCX)_2(PEt_3)_2]$ and trans-$[Pt(CH_3)I(PEt_3)_2]$

The complexes with acetylene ligands bound to platinum were deactivated with respect to addition-elimination reactions with silyl halides. SiH_4 showed no sign of reacting with $Pt(CCX)_2(PEt_3)_2$ (X = H, Ph) when equimolar proportions were mixed in benzene; for X = Ph the sample was heated to 323K in a sealed tube for five weeks without any reaction occurring. From equimolar proportions of SiH_3Br and $Pt(CCPh)_2(PEt_3)_2$, after three days at 313K, the ^1H spectrum showed one new silicon compound (singlet, τ = 6.03, $^1J(SiH)$ = 217.4 Hz) and a small amount of a Pt-SiH complex (τ = 5.83, $^2J(PtH)$ = 126.3 Hz, $^3J(PH)$ = 9.3 Hz). By analogy with the $SiH_3CCH/PtI_2(PEt_3)_2$ reaction, the silicon compound was probably $SiH_2Br(CCPh)$ and the complex trans-$[Pt(CCPh)[SiHBr(CCPh)](PEt_3)_2]$. SiH_3Br showed no signs of reaction with trans-$[Pt(CCCF_3)_2(PEt_3)_2]$.

In contrast, when a methyl group was substituted on the platinum, a very rapid reaction took place. In the reaction of SiH_3I with $Pt(CH_3)I(PEt_3)_2$ at room temperature in benzene, effervescence was complete within five minutes. The non-condensible gas was identified, from its infrared spectrum, as methane. The main product, identified by its n.m.r. parameters,

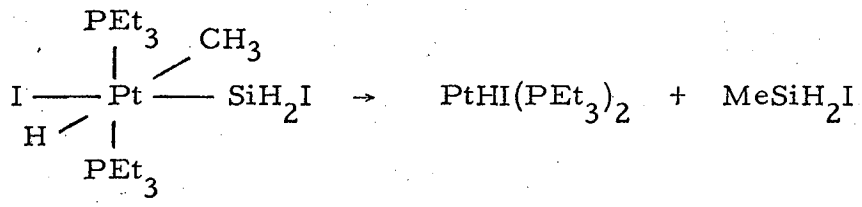
was $PtI(SiH_2I)(PEt_3)_2$ with small amounts of $CH_3.SiH_2I$ and $PtI(SiH_3)(PEt_3)_2$ also being produced. This agrees with the following scheme



CH_4 + $PtI(SiH_2I)(PEt_3)_2$

Acetylenic groups bound to Pt will have a significant degree of π bonding in the Pt-C bond. The effect of this will be to partially reduce the electron density on platinum and will be most pronounced when $-CF_3$ is bound to the acetylene. In contrast the σ -inductive effect of the methyl group should increase the electron density on the metal. This evidence lends support to the suggestion that the rate determining step in these addition-elimination reactions is the electrophilic attack by the Group IV atom on platinum.

The formation of $CH_3.SiH_2I$ in the above reaction is of interest. It could be formed by exchange between SiH_3I and the complex of H for CH_3 but is probably more likely to be produced by the breakdown of an isomeric form of the six-coordinated intermediate,



I

Attempts to prepare a pure sample of cis-$[Pt(CH_3)_2(PEt_3)_2]$ were unsuccessful so full characterisation of the reactions with silyl and germyl halides was not possible. However preliminary reactions with SiH_3I showed that there was very rapid evolution of methane and the formation of trans-$[PtI(SiH_2I)(PEt_3)_2]$. Large amounts of $CH_3.SiH_3$ along with some $(CH_3)_2.SiH_2$ and $CH_3.SiH_2I$ were also produced. The $CH_3.SiH_2I$ could be formed from a six-coordinated complex analogous to I but the methylsilanes must have resulted from exchange of I for CH_3 to give $CH_3.SiH_3$ and $Pt(CH_3)I(PEt_3)_2$. The reaction of HCl with cis-$[Pt(CH_3)_2(PEt_3)_2]$ has been reported;[91,92] this also produced methane but the product complex was cis-$[Pt(CH_3)Cl(PEt_3)_2]$.

CHAPTER 4

SILYL AND GERMYL COMPLEXES OF PALLADIUM

4.1. Introduction

Complexes in which palladium is directly bound to Group IV B elements, other than carbon, are rarer than the corresponding complexes of platinum; this is a result of their lower thermal, kinetic and/or thermodynamic stabilities.[51,93,94] The order of stabilities for Pd-Group IVB complexes is reported to be Ge > Pb ≫ Sn ~ Si[51] and until recently the only stable complexes reported have had R_3Ge[77,94,95] or R_3Pb[96] (R = organo or chloro group) bound to palladium. Solutions of complexes with palladium-silicon bonds have however been reported.[78] The complexes reported have trans configurations and all are of palladium (II). Octahedral complexes of platinum (IV) are well known but palladium is more reluctant to form Pd(IV) complexes. This has been ascribed largely to the fact that the sum of the first four ionisation potentials of palladium (109.5 eV) is greater than that of platinum (97.16 eV).[51,82,97,98]

The palladium-germanium bond has been formed by the action of Ph_3GeLi on trans-$[PdCl_2(PEt_3)_2]$.[77,94]

$$\text{trans-}[PdCl_2(PEt_3)_2] + 2Ph_3GeLi \xrightarrow[253K]{\text{Monoglyme}} \text{trans-}[Pd(GePh_3)_2(PEt_3)_2] + 2LiCl$$

I

The product was difficult to isolate because the Pd-Ge bond was

unstable to water and oxygen above 233K and decomposed thermally at 253K in solution. Above 370K the solid decomposed to give products typical of radical intermediates.

$$I \xrightarrow{370\text{-}380K} C_6H_6 + Ph_6Ge_2 + Ph_4Ge + Et_3P + C_2H_4 + H_2 + Pd$$

When other palladium complexes such as $PdCl_2(PPh_3)_2$, $PdCl_2$ (bipy.) or $PdCl_2(Ph_2P.(CH_2)_2.PPh_2)$ were treated with Ph_3GeLi the expected colour change took place but decomposition occurred during the isolation of the products. Using Ph_3PbLi the analogous complex containing Pd-Pb bonds was formed.[96] The Pd-Ge bond in I was cleaved by HCl to give, initially, trans$[PdCl_2(PEt_3)_2]$ and Ph_3GeH but these two products reacted further on heating to give a palladium hydride complex which decomposed to palladium metal. A detailed reaction mechanism has not been proposed, but in view of the reluctance of palladium (II) to undergo oxidation to palladium (IV), the reaction is thought to occur by direct cleavage of the Pd-Ge bond by HCl. Although hydrogen readily cleaves the Pt-Ge bond in triphenylgermylplatinum complexes,[40] only with 100 atmospheres of hydrogen over a week at room temperature does a similar reaction occur with I.[77]

$$I \xrightarrow[100\ atm.]{H_2} Pd(GePh_3)H(PEt_3)_2 + Ph_3GeH$$

The reaction was complicated by thermal decomposition of $Pd(GePh_3)H(PEt_3)_2$. It was possible to replace the Et_3P groups by 2 moles of cyanide without breaking the Pd-Ge bond.[77]

$$I + 2KCN \rightarrow 2Et_3P + Pd(CN)_2(GePh_3)_2$$

Excess potassium cyanide cleaved the metal-metal bond forming $K_2[Pt(CN)_4]$. The only other stable palladium-germanium complex reported is $Pd(C_6H_5NC)_2(GeCl_3)_2$.[95]

In preliminary studies of the action of SiH_3Cl on trans-$[PdCl_2(PEt_3)_2]$, Bentham[78] found that hydrogen was evolved and, by analogy with reactions of silyl halides with trans-$[PtCl_2(PEt_3)]$, the products trans-$[PdCl(SiH_2Cl)(PEt_3)_2]$ and trans-$[PdCl(SiHCl_2)(PEt_3)_2]$ formed. They were identified by their ^1H n.m.r. spectrum in benzene solution.

Hydrides of palladium (II) have been formed as unstable intermediates in some of the reactions discussed above; recently however several relatively stable palladium hydrides have been prepared. At one stage it was suggested[99] that neutral reducing agents were required to prepare these hydrides; this contrasts with the strongly basic or acidic environments used in the preparation of platinum hydrides. By the action of Me_3GeH on trans-$[PdCl_2(PEt_3)_2]$ at 313K in an evacuated, sealed system for several days, colourless prisms of trans-$[PdClH(PEt_3)_2]$ were formed.

$$PdCl_2(PEt_3)_2 + Me_3GeH \rightarrow H_2 + Me_3GeCl + Me_6Ge_2 + PdClH(PEt_3)_2 + \text{trace Pd.}$$

It was suggested that the reaction proceeded via a free radical mechanism. In the ^1H n.m.r. spectrum the Pd-H resonance was a singlet with no coupling to the two ^{31}P nuclei; the Et_3P group however did not give the resonance expected from a system with rapid phosphine exchange. (cf. Section 3.3.)

An equilibrium mixture of hydrides was produced by the reaction of trans-$[PdCl_2(PR_3)]$ (R = Et, Pr^n, Bu^n) with trans-$[Ni(BH_4)H(PCy_3)]$ (Cy = cyclohexyl) from which nickel and palladium hydrides were separated.[100] The proton resonances of these hydrides did show coupling between PdH and the ^{31}P nuclei in the molecules. A strongly acidic medium has been used to prepare palladium hydrides; $PdClH(PPh_3)_2$ was prepared by the action of HCl on $Pd(CO)(PPh_3)_3$ in ether solution.[101]

While the action of HCl on $PtClH(PEt_3)_2$ gave the six-coordinated adduct $PtCl_2H_2(PEt_3)_2$ which then slowly eliminated hydrogen (Chapter 2 and reference 31), no such intermediate was observed for palladium. The action of HCl on $PdClH(PEt_3)_2$ lead to cleavage of the Pd-H bond and formation of $PdCl_2(PEt_3)_2$ and hydrogen.[99] This reaction may proceed via a short-lived six-coordinated complex or by direct cleavage of the Pd-H bond. The reaction of HCl with palladium (O) complexes[101] to produce

$PdClH(PPh_3)_2$ was postulated to be an oxidative addition reaction. This mechanism has also been proposed[78] for the formation of $PdCl(SiH_2Cl)(PEt_3)_2$ and $PdCl(SiHCl_2)(PEt_3)_2$ because of the similarities between it and the platinum system. It should however be noted that, if the lifetime of the octahedral M(IV) intermediate is very short, the apparent differences between cleavage and addition-elimination mechanisms may be small.

4.2. Reactions of Silyl and Germyl Halides with trans-$[PdY_2(PEt_3)_2]$

This chapter is concerned with a study of the action of silyl and germyl halides on four-coordinated halide complexes of palladium (II). Since the analogous platinum system has been studied,[78] it was of interest to see whether similar reactions and products would be observed for the palladium complexes.

In general it was found that the reactions did give the same products as were found for platinum; there were, however, many minor differences in, for example, reaction rates and the stability of products. When equimolar proportions of SiH_3X and trans-$[PdY_2(PEt_3)_2]$ (X = H, halogen; Y = halogen) were mixed at room temperature in benzene, a reaction took place and hydrogen gas was evolved. When X = Y = Cl this reaction was fairly rapid and a mixture of chlorosilanes, silane and palladium-silyl complexes was formed. An attempt was made to isolate the solid products by evaporating the solvent; evaporation at room temperature left a

deeply coloured oil, but a pale yellow solid was obtained by evaporation of the solvent at 251K after O.5 hr. reaction. Characterisation by infrared and C,H analysis was inconclusive as the solid proved to be a mixture. The products were therefore identified by ^{1}H n.m.r. spectroscopy. When X = Y = Br, a similar but much more rapid reaction took place giving a mixture of bromosilanes and palladium-silyl complexes. Although the complexes were stable in solution, removal of the solvent, even at reduced temperatures, lead to rapid decomposition of the products; infrared spectra of solutions of the complexes could not be obtained due to decomposition in the spectrometer beam. In contrast to this increased reaction rate from Y = Cl to Br, when X = Y = I there was little sign of reaction; as was observed earlier,[78] the starting material decomposed slowly, to give metallic palladium.

Reaction of SiH_3X with trans-$[PdY_2(PEt_3)]$ (X = H, halogen, Y = halogen; $X \neq Y$) also gave a mixture of products which could not be isolated as pure solids. When X = H the reactions were considerably slower than with the halogens but the rates were still in the order for Y of $Cl < Br \gg I$. This reduction in reaction rate has been observed in the action of SiH_4 on platinum complexes[78] and was attributed to the rate determining step of the reaction involving electrophilic attack by silicon on the transition metal. For X = halogen, the first step in the reaction was rapid exchange of halogens to give the complex with the heavier halogen bound to

palladium. This was also observed for mixtures of silyl and platinum halides[78] and was explained in terms of relative energies of the metal-halogen bonds; E(Si-halogen) decreases in the order Cl > Br > I while E (Pt-halogen), though not well defined, probably decreases in the order I > Br > Cl. From thermodynamic data,[82] the order for E(Pd-halogen) also seems to be I > Br > Cl. When equimolar proportions of reactants were mixed, however, mixtures of $PdX_2(PEt_3)_2$, $PdXY(PEt_3)_2$ and $PdY_2(PEt_3)_2$ were obtained and these, on reaction with the silyl halide, gave a complex series of products.

The volume of hydrogen evolved from two of these reactions was measured; after three days reaction at 300K for X = Y = Br O.18 m.moles of hydrogen was obtained from O.21 m.moles of silyl bromide and for X = H, Y = Cl O.23 m.moles of hydrogen was obtained from O.27 m.moles of silane. Since effervescence had ceased it appears that these reactions did not go to completion.

The products of all the reactions discussed above were tentatively identified by ^1H n.m.r. spectroscopy. Complexes such as trans-$[Pd(SiH_2X)Y(PEt_3)_2]$ give Si-$\underline{H}$ resonances with a 1:2:1 triplet pattern ($^3J \simeq 14$ Hz) due to coupling with the two effectively equivalent ^{31}P nuclei; halosilanes were identified by known chemical shifts. The identity of the complexes was confirmed by comparison with platinum-silyl complexes.[78] The ^1H n.m.r. parameters are summarised in Table 4.1. For X = Y = Cl, Br, the solutions

darkened with time from yellow to red-brown; this darkening occurred after about 0.5 hr. for X = Y = Cl, but within minutes for X = Y = Br. Darkening of solutions of analogous platinum-silyl complexes was associated with broadening and ultimate collapse of the Si-H resonances; the proton resonances of the palladium-silyl complexes, however, remained sharp even if the solutions were kept at room temperature for several hours. In the proton spectrum of the $SiH_3X/PdY_2(PEt_3)_2$ reaction (X = Y = Cl), the triplet coupling due to ^3J(HSiPdP) ultimately collapsed; this is probably because decomposition liberated some free Et_3P which then induced rapid exchange of phosphorus ligands. A similar effect was observed in platinum-silyl complexes where free Et_3P caused collapse of ^3J(HSiPtP). For X = H, Y = Cl, no phosphorus-hydrogen coupling was observed for the products. Because of the slower reaction, small amounts of decomposition may have lead to traces of free Et_3P being produced before the products were formed. In contrast for X = Y = Br and X = H, Y = Br, the coupling ^3J(HSiPdP) did not collapse even after several days at room temperature. In complexes of the form trans-$[Pd(SiH_2X)Y(PEt_3)_2]$ the strength of the Pd-P bond will be affected by cis influences from $-SiH_2X$ and -Y; the above evidence suggests that this influence is greater for Y = Cl than for Y = Br. An attempt to stop the Et_3P exchange in the products of the reaction $SiH_4/PdCl_2(PEt_3)_2$, by removal of all the volatile materials from the reaction mixture after three days

Table 4.1. N.M.R. Parameters for trans-$[PdXY(PEt_3)_2]$ recorded at 300K in benzene/tetramethylsilane solution

X	Y	τ(M<u>H</u>) ppm	^3J(PH) Hz
SiH_3	Cl	6.88	n.o.
SiH_3	Br	6.66	9.5
SiH_2Cl	Cl	5.23	14.0
SiH_2Cl	Br	5.26	14.7
SiH_2Cl_2	Cl	4.28	n.o.
SiH_2Br[a]	Br	5.69	14.8
SiH_2Br_2[b]	Br	4.46	18.3
GeH_3	Cl	7.08	9.3
GeH_2Cl	Cl	4.93	12.5
GeH_2Br	Br	5.49	13.0
Estimated errors		$\pm$0.02	$\pm$0.5

The product $PdI(SiHXY)(PEt_3)_2$ (where probably X = Br, Y = I) from the $SiH_3Br/PdI_2(PEt_3)_2$ reaction had parameters,

$$\tau(\text{Si}\underline{\text{H}}) = 4.45 \text{ ppm}, \quad ^3J(PH) = 19.0 \text{ Hz}$$

Note: a. $\delta(^{31}P)$ for $PdBr(SiH_2Br)(PEt_3)_2$ was + 13.1 ppm to high frequency of 85% H_3PO_4

b. $\delta(^{31}P)$ for $PdBr(SiHBr_2)(PEt_3)_2$ was + 14.9 ppm.

reaction and replacing them with fresh solvent, was unsuccessful. The SiH proton resonances for the product complexes still did not show the triplet splitting due to $^{3}J(PH)$.

The progress of the reactions with time is summarised in Table 4.2. The palladium-silyl complexes observed were initially $Pd(SiH_2X)X(PEt_3)_2$ then later $Pd(SiHX_2)X(PEt_3)_2$ from the reaction of SiH_3X with $PdX_2(PEt_3)_2$ (X = Cl, Br) ; SiH_2X_2 was observed as an intermediate species. The reaction of SiH_4 with $PdX_2(PEt_3)_2$ (X = Cl, Br) was slower but gave similar types of products. These observations are consistent with an oxidative addition - elimination mechanism which, for X = Cl, is shown in Scheme 1. This mechanism does require the formation of a six-coordinated palladium (IV) complex as an intermediate. This species was not observed in any of the ^{1}H n.m.r. spectra studied; if, however, the formation of this complex is the rate determining step in the reaction (cf. platinum-silyl chemistry) and its breakdown is very rapid because of its instability, then it would not be observed. Further confirmation of this type of mechanism was obtained from the action of SiH_3X (X = H, Cl) on trans-$[PdCl_2(PEt_3)_2]$. A proton resonance at 23.57τ, which appeared on mixing the reactants and finally disappeared after about four days, has been assigned to trans-$[PdClH(PEt_3)_2]$; this intermediate is required by Scheme 1 as a breakdown product of the first six-coordinated palladium complex formed. The resonance was a

Table 4.2. Summary of Progress of Reactions with Time. (observed by ^1H n.m.r. spectroscopy).

Major Products Observed	Reactants							
	X = Cl				X = Br			
reaction considered	SiH_4/PdX_2L_2		SiH_3X/PdX_2L_2		SiH_4/PdX_2L_2		SiH_3X/PdX_2L_2	
reaction time	short	long	short	long	short	long	short	long
SiH_4	***	*	-	-	***	**	-	-
SiH_3X	-	-	***	-	-	-	***	-
SiH_2X_2	-	-	*	-	-	-	**	-
$Pd(SiH_3)XL_2$	-	***	-	-	-	**	-	-
$Pd(SiH_2X)XL_2$	-	**	*	-	-	**	**	*
$Pd(SiHX_2)XL_2$	-	**	-	***	-	-	-	***

***, **, * represents large, intermediate, small amounts of product.

L = Et_3P.

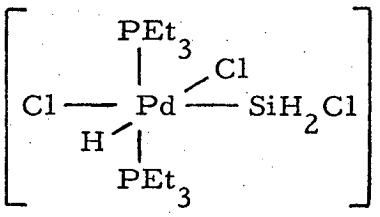
slightly broad singlet even when the low field peaks showed triplet patterns and it did not resolve into a multiplet on cooling the solution to 258K. For $SiH_3Cl/PdCl_2(PEt_3)_2$, an attempt to repeat this reaction in toluene to allow lower temperature studies gave the same low field resonances but no Pd-H resonance. The relative rates of formation and removal of this intermediate may have changed in the slightly more polar solvent. The resonance at 23.57T was not assigned to a palladium (IV) complex because (i) a fairly strong Si-H resonance would also be expected from this complex and none was observed, and (ii) the product giving rise to this signal was stable in solution for 3 - 4 days at 300K which is not consistent with present observed stabilities of six-coordinated palladium complexes. The action of SiH_3X (X = H, Br) on $PdBr_2(PEt_3)_2$ gave no evidence for the formation of trans-$[PdBrH(PEt_3)_2]$. If, as the products suggest, reaction Scheme 1 is followed, then the rate of step (b) must have increased relative to step (a) from the dichloride to the dibromide complexes.

The infrared spectrum of the solid products from the reaction $SiH_3Cl/PdCl_2(PEt_3)_2$ showed a collection of strong peaks due to ν(SiCl); it is possible that, in addition to the products given in Table 4.2, small amounts of trans-$[PdCl(SiCl_3)(PEt_3)_2]$ were formed by further reaction (Scheme 2).

In the initial stages of the reaction of SiH_3Br with $PdBr_2(PEt_3)_2$ several small singlet peaks appeared in the ^1H n.m.r.

Scheme 1.

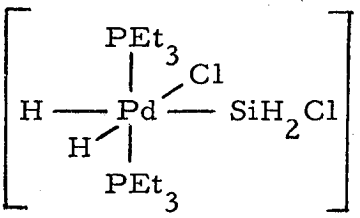
(a) SiH_3Cl + trans-$[PdCl_2(PEt_3)_2]$ →



or an isomer

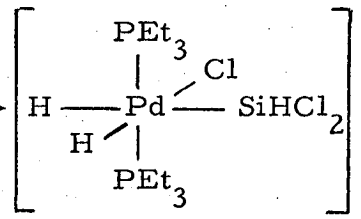
fast
→ trans-$[PdClH(PEt_3)_2]$ + SiH_2Cl_2

(b)(i) trans-$[PdClH(PEt_3)_2]$ + SiH_3Cl →



fast
→ trans-$[PdCl(SiH_2Cl)(PEt_3)_2]$ (I) + H_2

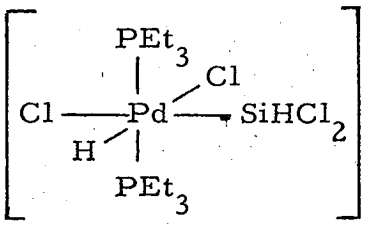
or (ii) trans-$[PdClH(PEt_3)_2]$ + SiH_2Cl_2 →



fast
→ trans-$[PdCl(SiHCl_2)(PEt_3)_2]$ (II) + H_2

Scheme 2.

(a) SiH_2Cl_2 + trans-$[PdCl_2(PEt_3)_2]$ →



or an isomer

→ trans-$[PdClH(PEt_3)_2]$ + $SiHCl_3$

(b) $SiHCl_3$ + trans-$[PdClH(PEt_3)_2]$ → trans-$[PdCl(SiCl_3)(PEt_3)_2]$ + H_2

spectrum in the region of 5-6 τ. They appeared before any palladium-silyl complex was formed and disappeared in times ranging from minutes to days. They have not been identified but may be due to some intermediate silyl compounds.

As mentioned earlier the reaction of SiH_3X with $PdY_2(PEt_3)_2$ ($X \neq Y$) lead to a complex mixture of products. When X = Br, Y = Cl or X = Cl, Y = Br, the product trans-$[PdBr(SiH_2Cl)(PEt_3)_2]$ was identified from its ^1H n.m.r. spectrum. The chemical shift of Si-H in this complex, however, is very similar to that in the complex trans-$[PdCl(SiH_2Cl)(PEt_3)_2]$ since the change of a ligand three atoms removed from the proton in general has little effect on its environment. Thus the absolute identification of products in these 'mixed' reactions was difficult. When X = Br, Y = I, a very slow reaction took place to give a weak triplet in the n.m.r. spectrum. This could only be assigned to a product of the form trans-$[PdI(SiHXY)(PEt_3)_2]$ (X, Y = Br, or I). No reaction was observed when X = Cl, Y = I.

The reactions of GeH_3X (X = H, halogen) with $PdY_2(PEt_3)_2$ (Y = halogen) were similar to the reactions of germyl halides with complexes of the form $PtHY(PEt_3)_2$; the products from the latter decomposed more readily that the corresponding platinum-silyl complexes due to their lower thermal stability. In all cases only the first product formed trans-$[Pd(GeH_2X)Y(PEt_3)_2]$ (X = H, Cl, Br; Y = Cl, Br) was detected before decomposition. They are tabulated,

with their n.m.r. parameters, in Table 4.1. Trans-$[PdHX(PEt_3)_2]$ (X = halogen) was not observed but, from the products and intermediate germyl species detected, Scheme 1 seems to have been followed. The instability of the products made it impossible to isolate the solids for further characterisation.

4.3. Reaction of SiH_3Br with trans-$[PtBr_2(PEt_3)_2]$

This reaction was studied partly to complete the series of reactions started by Bentham[78] and partly to use as a comparison with the above system. The presence of ^{195}Pt gives added information about the types of products formed. The magnitude of the coupling $^2J(PtSiH)$ is very sensitive to the number of halogens bound to the silicon atom; it increases by approximately a factor of two in the change from Pt-SiH_2X to Pt-$SiHX_2$.

The reaction was fast, with rapid evolution of hydrogen, and resulted in a yellow solution with a small amount of precipitate. Effervescence ceased after about one hour and the products were stable in solution for at least four days at room temperature. The two products, trans-$[PtBr(SiH_2Br)(PEt_3)_2]$ and trans-$[PtBr(SiHBr_2)(PEt_3)_2]$ were formed; their n.m.r. parameters are given below,

	τ(SiH)ppm	^2J(PtH)Hz	^3J(PH) Hz
$PtBr(SiH_2Br)(PEt_3)_2$	5.87	125.2	9.3
$PtBr(SiHBr_2)(PEt_3)_2$	4.29	244.4	11.2

Neither trans-$[PtBrH(PEt_3)_2]$ nor any six-coordinated complexes of platinum was detected.

CHAPTER 5

PREPARATION AND PROPERTIES OF MH_3CCCF_3

SiH_3CCH has been prepared and characterised and its reactivity towards platinum complexes has also been studied (Chapter 3). It was therefore of interest to prepare SiH_3CCCF_3, in which the acetylene has been substituted with a strongly electron-withdrawing group, and to study the effect of this on the properties of this compound and, in particular, its reactivity towards platinum complexes (Chapter 3).

The first attempt to prepare this compound was by an analogous reaction to the one used to prepare SiH_3CCH.

$$2Na + 2HCCCF_3 \xrightarrow[227K]{\text{ammonia}} 2NaCCCF_3 + H_2$$

$$NaCCCF_3 + SiH_3Br \xrightarrow[3OOK]{\text{diglyme}} SiH_3CCCF_3 + NaBr$$

The change in colour of the ammonia solution from blue to red indicated that $NaCCCF_3$ had been formed, but when SiH_3Br was condensed onto the diglyme solution a very vigorous reaction, with effervescence, took place. An infrared spectrum of the volatile materials from this reaction showed that only SiH_4, SiH_3Br and $HCCCF_3$ had been produced. SiH_3CCCF_3 was successfully prepared by using a Grignard reagent instead of the sodium salt of trifluoro-methylacetylene.

$$IMgMe + HCCCF_3 \xrightarrow[\text{reflux}]{\text{ether}} IMg(CCCF_3) + CH_4$$

$$IMg(CCCF_3) + SiH_3Br \xrightarrow[300K]{\text{diglyme}} SiH_3CCCF_3 + IMgBr$$

$IMg(CCCF_3)$ reacted smoothly with SiH_3Br over 0.5 hr. at room temperature; yields of 40-60% of SiH_3CCCF_3 were obtained. $CH_3.SiH_3$, $HCCCF_3$, $(C_2H_5)_2O$ and SiH_3Br, all possible impurities in this reaction, have vapour pressures similar enough to that of SiH_3CCCF_3 to make separation by fractional condensation difficult. Steps were therefore taken to minimise the quantities of those produced. By using a slight excess of $HCCCF_3$ all the MeMgI (from which $MeSiH_3$ was produced by reaction with SiH_3Br) was removed. Pumping on the solution of $IMg(CCCF_3)$ in diglyme removed excess $HCCCF_3$ and $(C_2H_5)_2O$ then adding slightly less than equimolar proportions of SiH_3Br minimised the quantities of excess bromide. GeH_3CCCF_3 was produced by the same technique but using GeH_3Cl instead of the bromide; a considerably faster reaction took place when chloride was used. Small quantities of Ge_2H_6 were also formed in this reaction.

These compounds were characterised by n.m.r. infrared and mass spectroscopy, their molecular weight in the gas phase (exact mass technique) and their vapour pressure curves. The structure of SiH_3CCCF_3 in the gas phase has also been determined

by electron diffraction; this is discussed fully in Chapter 6.

The ^{1}H and ^{19}F (for M = Si) n.m.r. spectra of pure MH_3CCCF_3 showed single resonances with quartet splittings (^{5}J = 1.7 = 1.8 Hz) due to the five bond H....F coupling. Long range couplings involving acetylene, allene and cumulene systems are well known[102]. The Fermi contact term alone does not account for the magnitude of these couplings; transmission of spin information via the π-electron system must also be involved. Because of the separation of the two coupled nuclei (5 - 6Å), 'through space' coupling will not be involved. The parameters obtained are given in the table below.

	τ^{a} ppm	$\delta(^{19}F)$ ppm[b]	^{5}J(HF) Hz
SiH_3CCCF_3[c]	6.09	-53.0	1.7
GeH_3CCCF_3[c]	5.89	n.o.	1.8

a. Relative to Me_4Si at 10.00τ

b. " " CCl_3F

c. Measured in CCl_3F/Me_4Si solution

The infrared spectra have been recorded in the gas phase and for M = Si in the solid phase. The principal maxima of all the observed bands are given in Table 5.1. The bands due to M-H stretching and deformation modes of vibration and those due to CF_3 stretching modes can be assigned with reasonable certainty but other

assignments are more tentative. Unfortunately, for M = Si, $\nu(C\equiv C)$ coincided with the symmetric and asymmetric SiH stretching modes; in the solid phase spectrum three bands were observed in the region of 2000 cm^{-1} but deuteration would be required to differentiate between them. For M = Ge a shift in the M-H bands to low frequency left $\nu(C\equiv C)$ at 2218 cm^{-1}. The M-H bands show rotational detail; this is consistent with an MH_3 group which has a very low barrier to internal rotation about the molecular axis.

The mass spectra for these compounds have been recorded but, due to the presence of small amounts of inseparable impurities, it was not possible to obtain a complete breakdown pattern. For M = Si, the expected range of peaks due to loss of protons from the parent ion (mass numbers 121 - 125) was observed. The other major breakdown products were those formed by cleavage of the remaining single bonds in the molecule - SiH_3^+, $CCCF_n^+$, CF_n^+, SiH_3CC^+, $SiH_3CCCF_2^+$ and SiH_3CCCF^+ (n = 3, 2, 1).

Only small amounts of CCF_3^+, produced by cleavage of the triple bond, were produced. For M = Ge, the germanium isotope pattern for the parent ion was prominent (mass numbers 171 - 163). In other respects this molecule showed the same tendency, although to a lesser extent, for cleavage of single bonds. From the mass spectra the exact masses of several ions of each compound were determined to confirm their identity.

Table 5.1. Infrared Data for MH_3CCCF_3

SiH_3CCCF_3 gas	SiH_3CCCF_3 solid	GeH_3CCCF_3 gas	Assignments
2202 m.s.[a]	2221, 2214, 2202 m.s.	2218 m 2126 s[a]	$\nu(C\equiv C)$ $\nu(MH)$
1268, 1260 v.s.	1276, 1250 s.	1255 v.s.	$\nu(CF_3)$
1219, 1213 m	1218, 1205 m	1218 m	$\nu(CC)$
1176 v.s.	1142 v.s. (broad)	1167 v.s.	$\nu(CF_3)$
920 m[a] 914 s	938 m 915, 897 s	888 m[a] 822 s	$\delta(MH)$
685 m[a]	673 s	627 m[a]	ρ (MH)
613 w	608 m		$\delta(CF_3)$
346 m.w.	344 m.w.	320 w	ρ (CF_3)
312 w		268 m	δ(CCC)
235 w	240 w	235 w	δ(MCC)

Note:- a - average band centres

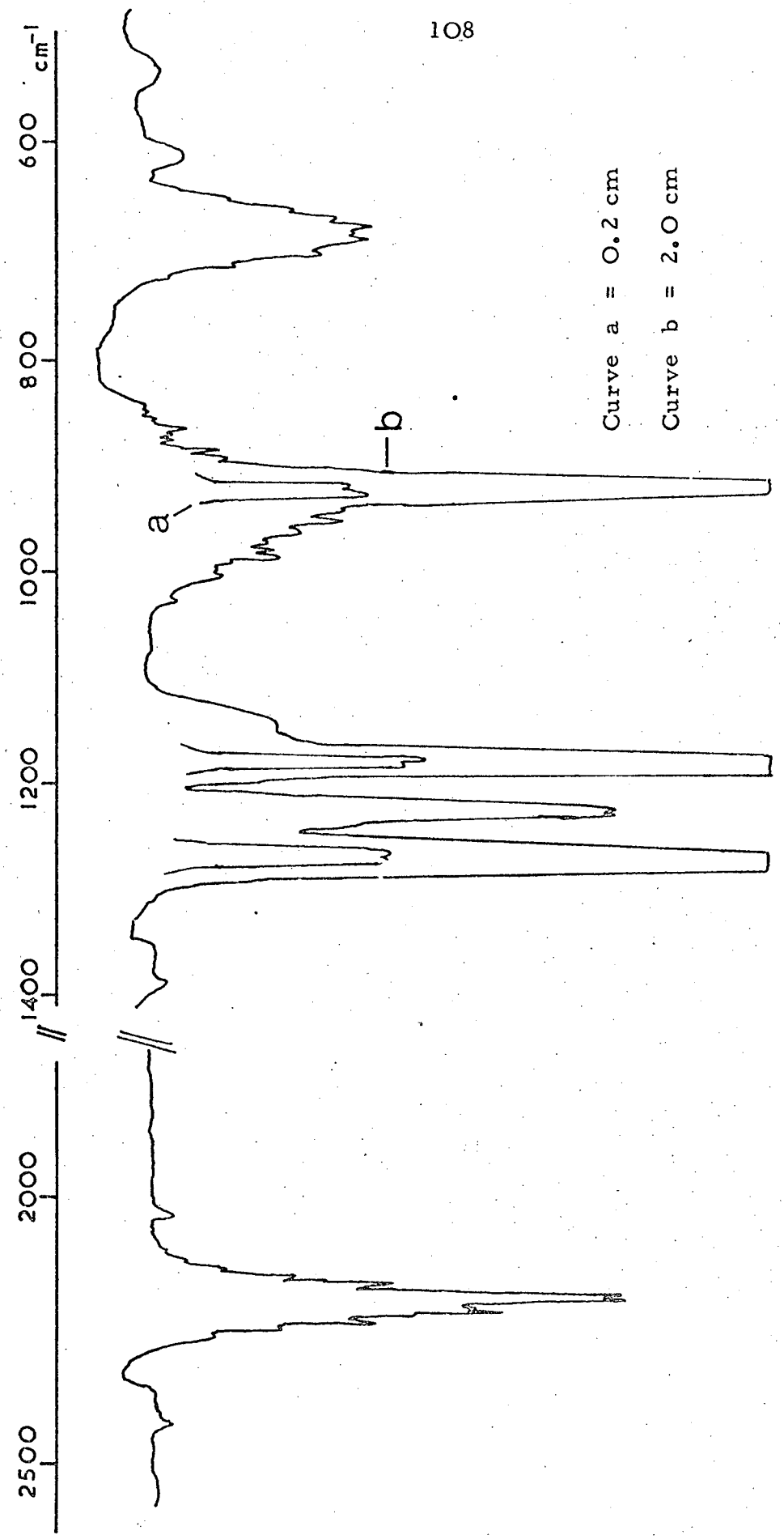


Fig. 5.1. Gas phase infrared spectrum of SiH_3CCCF_3

These are shown below,

	Mass found	Mass Expected	Error
$^{28}SiCCCF_3^+$	120.972156	120.972136	1 ppm
$^{28}SiHCCCF_3^+$	121.979780	121.979960	1.5 ppm
$^{28}SiH_2CCF_3^+$	122.987524	122.987785	2 ppm
$^{74}GeCCCF_3^+$	166.916407	166.916345	1 ppm
$^{72}GeH_2CCCF_3$	166.932745	166.932556	1.1 ppm

The vapour pressures of these compounds were measured over the temperature range 190 - 253K for SiH_3CCCF_3 and 213 - 253K for GeH_3CCCF_3. The values obtained, when plotted in the $\log_{10} p/ 1/T$ form, gave a linear relationship over the temperature range studied. The table of results is given in the experimental section; the parameters obtained from these measurements are summarised in Table 5.2. The melting point for SiH_3CCCF_3 was determined as 146 ± 1K.

Table 5.2. Parameters Obtained from Vapour Pressure Measurement

SiH_3CCCF_3

The relationship between vapour pressure and temperature between 190 K and 253 K is expressed by the equation,

$$\log_{10} p\,(cm) = -1320/T + 6.695$$

Boiling Point	274.0 ± 3.8 K
Latent Heat	25.2 ± 0.4 kJ mole^{-1}
Trouton's Constant	91.9 J mole^{-1} K^{-1}

GeH_3CCCF_3

The relationship between vapour pressure and temperature between 213 K and 253 K is expressed by the equation,

$$\log_{10} p\,(cm) = -1710/T + 7.705$$

Boiling Point	294 ± 6 K
Latent Heat	32.7 ± 0.6 kJ mole^{-1}
Trouton's Constant	111.2 J mole^{-1} K^{-1}

CHAPTER 6

MOLECULAR STRUCTURES OF METHYL PSEUDOHALIDES AND SILYL ACETYLENES BY ELECTRON DIFFRACTION

6.1. Introduction

Gas phase electron diffraction data for CH_3NCS, CH_3N_3, SiH_3CCH and SiH_3CCCF_3 were obtained using the Balzer's KD.G2 apparatus at the University of Manchester Institute of Science and Technology. The analysis of the data is presented in this chapter.

Interest in the structures of the methyl pseudohalides stems from the structures found for their silyl, germyl and difluorophosphino analogues. Silyl isocyanate and silyl isothiocyanate have been found from microwave[103, 104] and vibrational spectroscopy[105] to have linear heavy atom skeletons, whereas when studied by electron diffraction they appear to be bent at nitrogen.[106] In view of the large shrinkage corrections that must be applied in these cases the electron diffraction results are probably consistent with the spectroscopic results. In silyl azide[107] and the germyl[108, 109] and difluorophosphino[110] pseudohalides both microwave spectroscopy and electron diffraction show that the skeletons are bent.

(p - d)π bonding is widely held to be at least partly responsible for the linear structures of the silyl compounds but it is not certain whether this bonding affects the structures of the germyl and difluorophosphino compounds. Photoelectron spectroscopy provides some evidence that the bonding in these compounds includes some (p - d)π contribution.[111, 112] It was therefore of interest to study the methyl pseudohalides as these systems cannot have (p - d)π

bonding. Methyl azide was investigated by electron diffraction in 1937[113] and a partial structure has been determined for methyl isothiocyanate by microwave spectroscopy.[114,115] A full structure determination of methyl isocyanate was done[116] at the same time as the work reported in this chapter. The MNC angle for M = CH_3 was narrower than for M = SiH_3 and it has been suggested that this may be due at least in part to (p - d)π bonding; the angle observed however was very similar to those for M = GeH_3 and PF_2.

The structures of silyl acetylene and silyl perfluoropropyne were of interest because of the reported structures of silyl cyanide and silyl acetylene. Two preliminary microwave structures of silyl cyanide have been reported.[117,118] From this data the Si - C bond length can be estimated as about 1.848Å using reasonable estimates for other geometrical parameters in the molecule. In silyl acetylene a value of 1.826Å for the Si - C bond length has been found in two independent r_s structures.[119,120] In contrast the lengths of the H_3C - C≡ bond in methyl cyanide and methyl acetylene are essentially identical.[121] A recent investigation of the molecular structure of silyl cyanide by electron diffraction has confirmed the Si - C bond length as 1.848Å.[122] In the study of the structure of silyl perfluoromethylacetylene the effect of the electron-withdrawing $-CF_3$ group on the Si - C and C≡C bond lengths has been investigated.

6.2. Structures of Methylazide and Methylisothiocyanate

During the exposures, the samples of compounds were maintained at 273K (CH_3N_3) and 315K (CH_3NCS) with a nozzle temperature of 333K. Nozzle-to-plate distances of 500 and 1000 mm for CH_3NCS and 250 and 500 mm for CH_3N_3 were used giving ranges in the scattering variable s of about 1 - 16A^{o-1} and 2-30A^{o-1} respectively; the other two plates, 250 mm (CH_3NCS) and 1000 mm (CH_3N_3), were discarded because of poor data. The data were analysed as described in Chapter 7. The weighting functions (used to set up the off-diagonal weight matrix and defined as in reference 123), correlation parameters and scale factors are given in Table 6.1. The intensity and final weighted difference molecular intensity curves are shown in Figures 6.1 and 6.2.

For the molecular model, the assumptions made about the structures of CH_3NYZ and which were imposed as restrictions on the least squares refinements, were that the methyl group had local C_{3v} symmetry and that the NYZ group was linear. Geometrical parameters chosen to define the structure were bonded distances C-H, C-N, N-Y, Y-Z, angles HCN and CNY, the angle of twist of the methyl group with respect to the NYZ group, and the angle of tilt of the methyl group, and the angle of the tilt of the methyl group with respect to the C-N bond. The twist angle was defined to be zero when one hydrogen atom was staggered with respect to the lone pair on the nitrogen and therefore eclipsed with respect to the NYZ

Table 6.1. Weighting Functions, Correlation Parameters and Scale Factors

Compound	Camera Height (mm)	ΔS	S_{min}	S_1	S_2	S_{max}	P/h	Scale Factor	Wavelength
CH_3NCS	500	2	36	50	136	156	0.4313	0.733 ± 0.019	0.05659
	1000	1	12	25	62	75	0.4918	0.678 ± 0.022	0.05659
CH_3N_3	250	4	56	110	260	300	0.3942	0.690 ± 0.022	0.05659
	500	2	26	45	130	160	0.4929	0.818 ± 0.017	0.05659

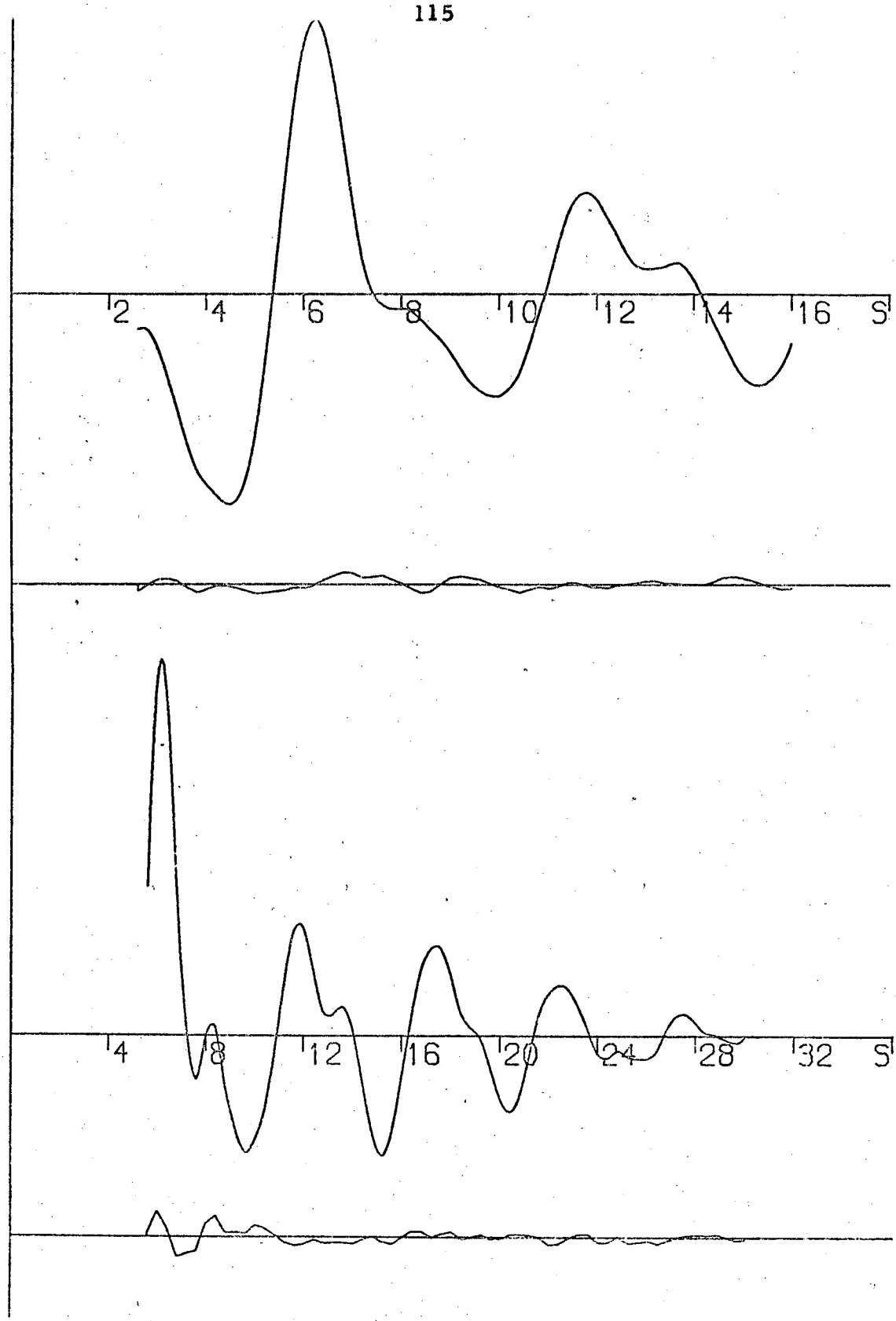


Fig. 6. 1. Methylazide intensity data.

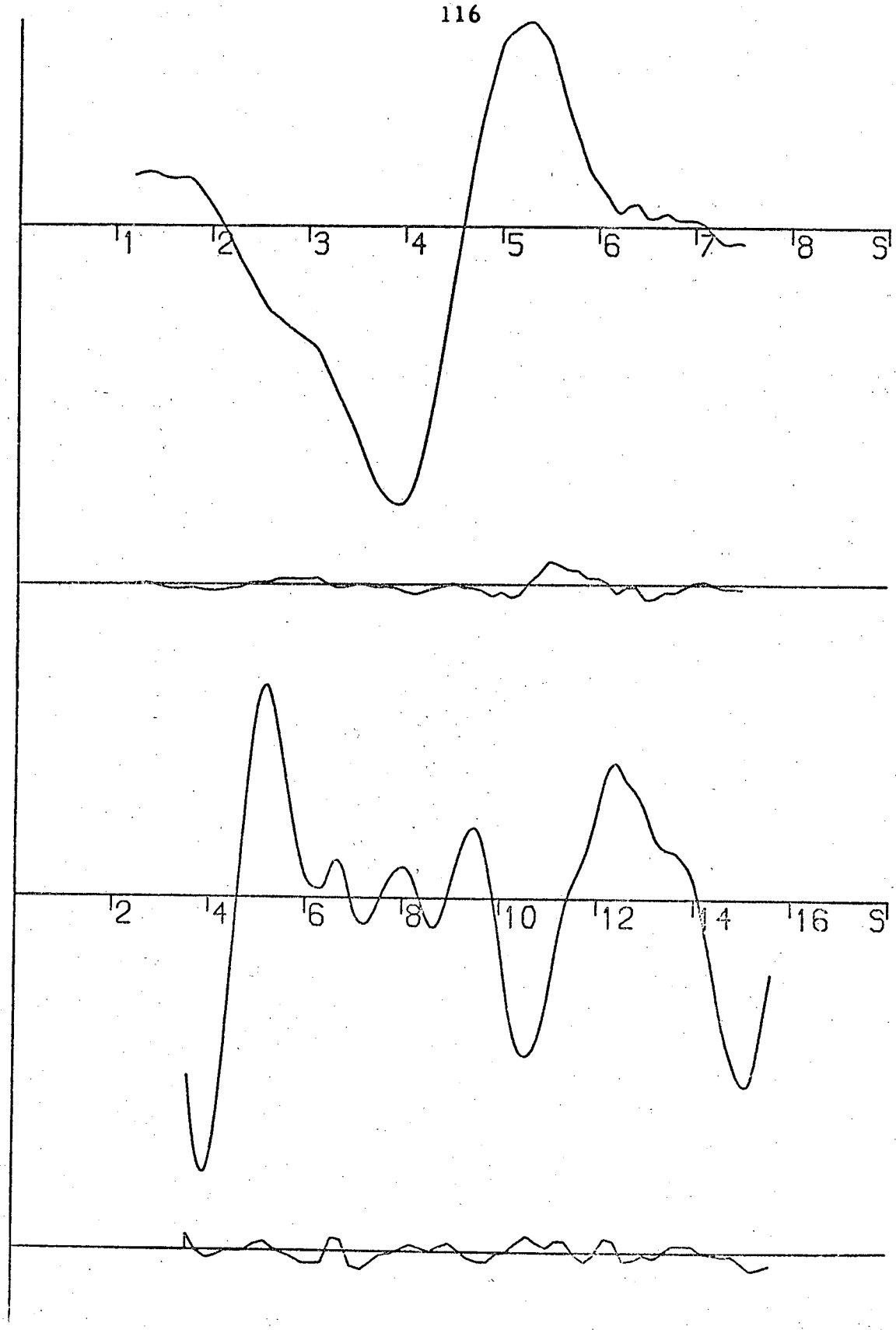


Fig. 6.2. Methylisothiocyanate intensity data.

group. The tilt angle was defined as the angle between the C_3 axis of the methyl group and the C-N bond. It was assumed that any tilt of the methyl group was in the plane of the CNYZ skeleton. The tilt was taken to be positive when the axis was tilted away from the NYZ group.

Methylazide refinement. Satisfactory refinements were carried out on the C-H, C-N, N-N and N-N' distances as well as the CNN angle and the amplitudes of vibration of the C-N bonded and both the C...N non-bonded atom pairs. Since the C-H and both the N-N bonded distances overlapped in the radial distribution curve (Figure 6.3), the amplitudes of the C-H and both the N-N vibrations were fixed at typical values.[124] Overlap of the shorter C...N non-bonded peak and the non-bonded N...N peak also occurred so that the N....N amplitude of vibration was also fixed at a typical value. Amplitudes of vibration of all the X...H non-bonded distances were also fixed since they contributed little to the total scattering intensity.

The HCN angle, the angle of twist and the angle of tilt were each found by doing a series of refinements with different fixed values of the angles and comparing the R factors for the various refinements. These angles would not refine in the normal way because of correlations with other parameters, and even by this method the HCN angle could not be determined. However, the methyl group was

found to be twisted by 25 ± 6^{o} from the eclipsed conformation and tilted by 3 ± 5^{o} away from the NNN chain.

Methylisothiocyanate refinement. The C-H, C-N, N-Cand C-S distances, the CNC angle and the amplitudes of vibration for the atom pairs N-C, C...S, C....C and S....N refined satisfactorily. In addition the C-N amplitude of vibration refined with the C-S amplitude tied at a constant ratio to it. This was necessary as the C-N and C-S peaks overlapped in the radial distribution curve (Figure 6.4). Typical values[124] were assumed for the amplitudes of vibration associated with the C-H, H...H, N....H, C....H and S....H atom pairs. The angle of twist, angle of tilt and the HCN angle were determined, as in the azide, as follows: HCN = 110 ± 9^{o}, twist angle = 54 ± 6^{o}, and the tilt angle = -0.7 ± 1.5^{o}.

Final parameters for these compounds are given in Tables 6.2 and 6.3. The estimated standard deviations quoted in the table include the random errors, determined in the least squares analysis, and allowances have been made both for systematic errors and for any constraints applied during the refinements. The final least squares correlation matrices are given in Table 6.4. The lowest R factors (R_g)[125] were 0.13 (CH_3N_3) and 0.15 (CH_3NCS).

A comparison of the MNY angle in the compounds PF_2NYZ, GeH_3NYZ, SiH_3NYZ and CH_3NYZ is given in Table 6.5. The anticipated wider angles in the compounds in which there may be

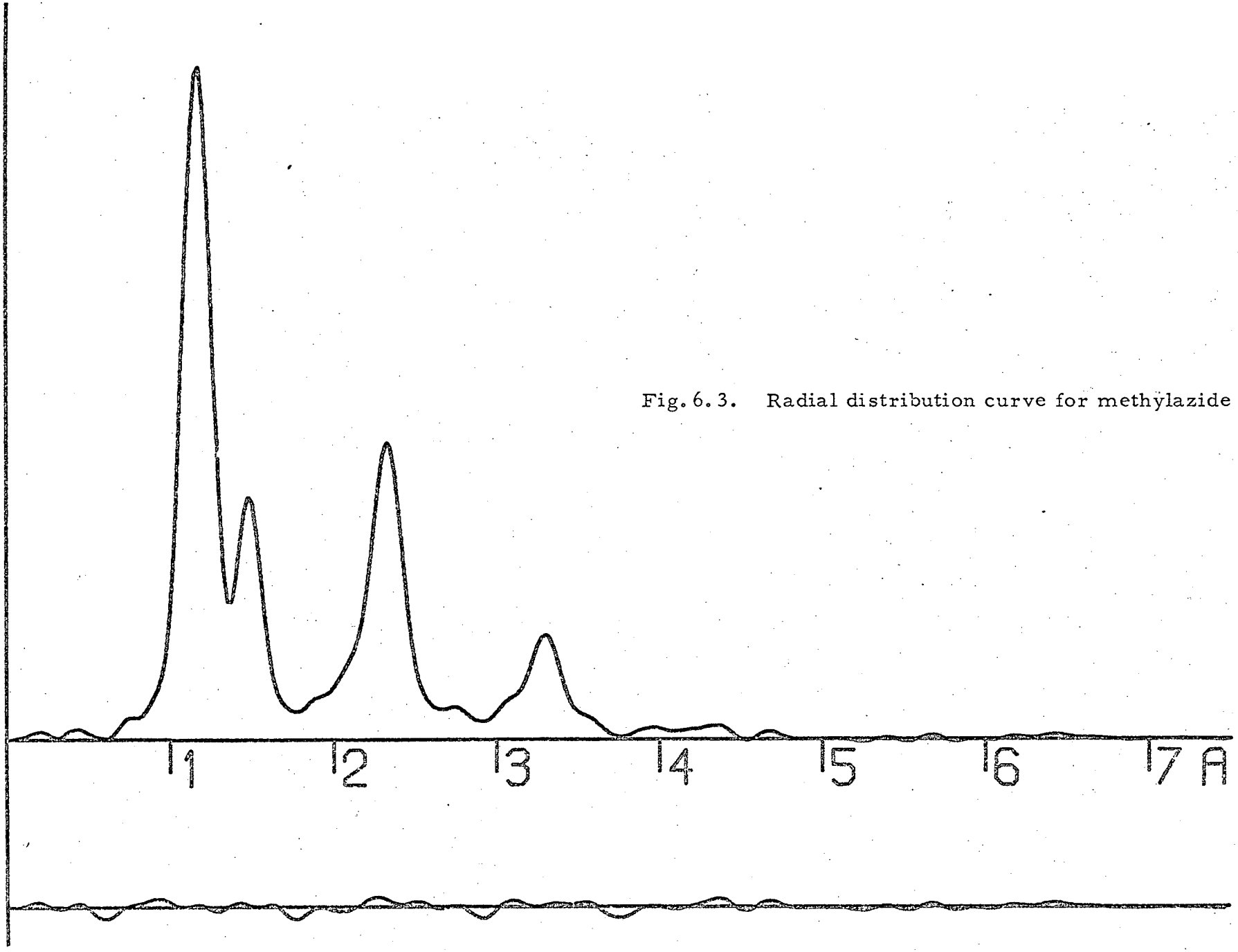


Fig. 6.3. Radial distribution curve for methylazide

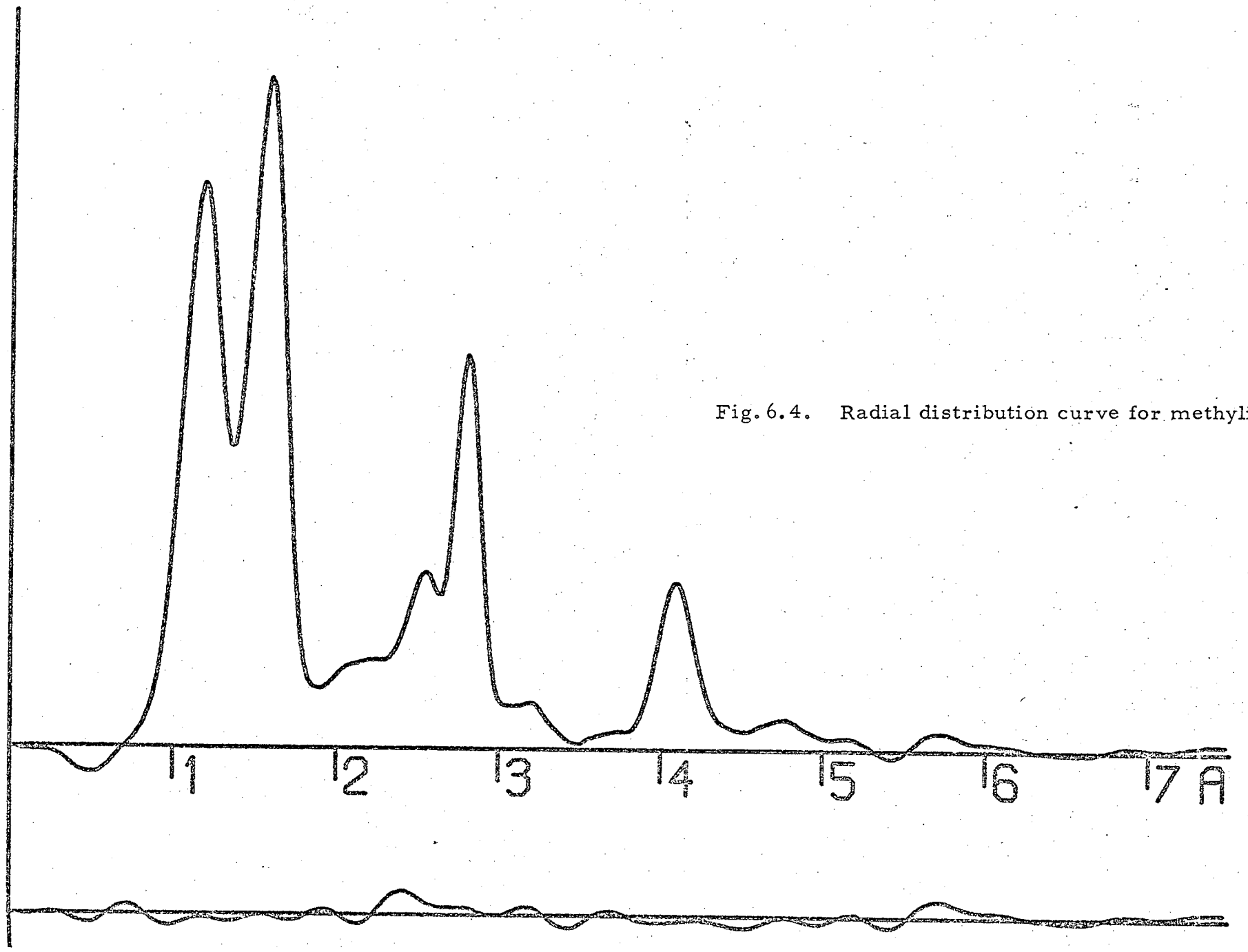
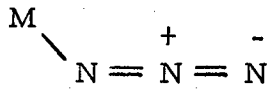
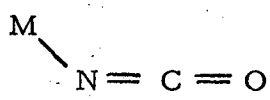


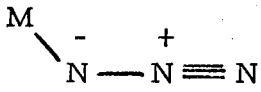
Fig. 6.4. Radial distribution curve for methylisothiocyana

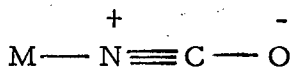
(p-d)π bonding are not always found. Some CH_3NYZ angles are larger than those in the F_2P- or H_3Ge- analogues while others are slightly smaller or very similar. These may be compared with the H_3Si- analogues which do have wider angles, probably due at least in part to (p-d)π bonding.

Methyl azide is similar to germyl azide in that the angle is smaller than in the corresponding isocyanate. This can be accounted for by considering the possible valence bond structures for the MNYZ group.









One of the valence bond structures for MNCO involves linear co-ordination at nitrogen, whereas in the azide both the structures are bent. Therefore on average the azide will be more bent than the isocyanate.

These valence bond structures can also be used to account for the N=C and C=S bond lengths. The N=C bond in methyl isothiocyanate is shorter than in most similar compounds, while the C=S bond is similarly unusually long. If M is electron releasing, as CH_3- is, then the linear $M-\overset{+}{N}\equiv C-\overset{-}{Z}$ structure will be

Table 6.2. Molecular Parameters for $CH_3NC'S$

A. Independent Distances

		Distance	Amplitude
r1	(C-H)	1.080 (fixed)	0.055 (fixed)
r2	(C-N)	1.479 ± 0.008	0.054 ± 0.011
r3	(N-C')	1.192 ± 0.006	0.055 ± 0.013
r4	(C'-S)	1.597 ± 0.005	0.049 ± 0.011

B. Dependent Distances

d5	(N...S)	2.783 ± 0.013	0.037 ± 0.019
d6	(C...C')	2.525 ± 0.016	0.066 ± 0.029
d7	(C...S)	4.047 ± 0.017	0.084 ± 0.012
d8	(H...H)	1.763 ± 0.007	0.110 (fixed)
d9	(N...H)	2.104 ± 0.011	0.120 (fixed)
d10	(N...H)	2.104 ± 0.011	
d11	(N...H)	2.104 ± 0.011	
d12	(C'...H)	3.187 ± 0.015	0.140 (fixed)
d13	(C'...H)	2.791 ± 0.013	
d14	(C'...H)	3.150 ± 0.015	
d15	(S...H)	4.713 ± 0.018	0.231 (fixed)
d16	(S...H)	4.086 ± 0.012	0.180 (fixed)
d17	(S...H)	4.657 ± 0.018	0.231 (fixed)

C. Independent Angles

1	(C-N-S)	$141.6^\circ \pm 0.3^\circ$
2	(N-C-H)	$110^\circ \pm 9^\circ$
3	(twist)	$54^\circ \pm 6^\circ$
4	(tilt)	$-0.7 \pm 1.5^\circ$

D. Dependent Angles

6	(H-C-H)	$109.3^\circ \pm 0.2^\circ$

Table 6.3. Molecular Parameters for $CH_3NN'N''$

A. Independent Distances

		Distance	Amplitude
r1	(C-H)	1.087 ± 0.014	0.055 (fixed)
r2	(C-N)	1.468 ± 0.005	0.047 ± 0.007
r3	(N-N')	1.216 ± 0.004	0.039 (fixed)
r4	(N'-N")	1.130 ± 0.005	0.035 (fixed)

B. Dependent Distances

d5	(N...N")	2.338 ± 0.009	0.057 (fixed)
d6	(C...N')	2.290 ± 0.006	0.061 ± 0.011
d7	(C...N")	3.273 ± 0.009	0.068 ± 0.011
d8	(H...H)	1.761 ± 0.022	0.110 (fixed)
d9	(N...H)	2.079 ± 0.013	
d10	(N...H)	2.143 ± 0.013	0.101 (fixed)
d11	(N...H)	2.115 ± 0.013	
d12	(N'...H)	3.087 ± 0.016	
d13	(N'...H)	2.468 ± 0.011	0.140 (fixed)
d14	(N'...H)	2.757 ± 0.013	
d15	(N"...H)	4.103 ± 0.015	
d16	(N"...H)	3.159 ± 0.007	0.180 (fixed)
d17	(N"...H)	3.605 ± 0.011	

C. Independent Angles

1	(C-N-N')	$116.8^\circ \pm 0.2^\circ$
2	(N-C-H)	110.7° (fixed)
3	(twist)	$25^\circ \pm 6^\circ$
4	(tilt)	$-3^\circ \pm 5^\circ$

D. Dependent Angles

5	(H-C-H)	$108.22^\circ \pm 0.0^\circ$

Table 6.4. Least Squares Correlation Matrices for a) CH_3NCS and b) CH_3N_3, multiplied by 1000

a.

r2	r3	r4	2	u2	u3	u6	u7	u14	k1	k2
1000	568	-310	-527	428	-45	27	142	177	-49	-10
	1000	-93	-746	67	-83	-4	-7	-10	-32	-100
		1000	-306	-250	434	13	-249	-238	158	136
			1000	-33	-117	-56	-30	18	-35	-10
				1000	324	255	120	364	569	118
					1000	168	-47	124	466	170
						1000	176	249	400	103
							1000	793	172	111
								1000	424	148
									1000	152
										1000

b.

r1	r2	r3	r4	2	u2	u6	u7	k1	k2
1000	252	184	-771	242	-388	-80	119	-551	456
	1000	167	-134	-421	-158	-25	201	-209	0
		1000	-330	-573	-162	102	228	398	157
			1000	-270	312	9	-252	236	290
				1000	-20	-75	-266	-385	-340
					1000	49	8	302	140
						1000	49	199	152
							1000	234	171
								1000	404
									1000

Table 6.5. Valence Angles at Nitrogen in Some Pseudohalides

Compound	Angle	Method of Determination	Reference
CH_3NCO	140°	ED	116
CH_3NCS	142°	ED	-
CH_3N_3	117°	ED	-
SiH_3NCO	180°	MW	103
	152°	ED	126
SiH_3NCS	180°	MW	104
	170°	ED	126
SiH_3N_3	<180°	MW	107
	126°	ED	126
GeH_3NCO	141°	ED	108
GeH_3N_3	119°	ED	108
PF_2NCO	131°	ED	110
PF_2NCS	141°	ED	110

[a] ED = electron diffraction, MW = microwave.

stabilised relative to the other forms. This leads to a lengthening of the C=S bond, a shortening of the N=C bond and a widening of the MNC angle. Similar observations were made about the structure found for methyl isocyanate.[116] In general, therefore, wide angles in pseudohalides may be associated with either (p-d)π bonding or an electron releasing group M.

The twist angle in these compounds is determined by two main repulsive forces - that between the methyl hydrogen atoms and the lone pair on the nitrogen in CH_3NYZ, and that between the hydrogen atoms and the NYZ group. In methyl azide, which has a twist angle of about 25^{o}.these two repulsions must be of similar magnitude (since a twist angle of 28.65^{o} is the one expected if these two repulsive forces are equal) whereas in methyl isothiocyanate the NCS - H repulsion seems to be dominant, giving a structure with one hydrogen atom almost eclipsing the lone pair on the nitrogen. The small negative tilt in methyl azide is consistent with the greater interaction between the nitrogen lone pair and the methyl group in this compound than in the others.

6.3. Structures of Sily Acetylene and Silyl Trifluoromethylacetylene

During the exposures the samples of compounds were maintained at 209K (SiH_3CCH) and 228K(SiH_3CCCF_3) with a nozzle temperature of 333K. Nozzle-to-plate distances of 500 mm for SiH_3CCH and 250 mm and 500 mm for SiH_3CCCF_3 were used;

these gave ranges in the scattering variable s of 2-16$\mathring{A}^{-1}$ and 2-30$\mathring{A}^{-1}$ respectively.

The other plates were discarded because of poor data. The weighting functions, correlation parameters and scale factors are given in Table 6.6. The intensity and final weighted difference curves are shown in Figures 6.5 and 6.6.

The assumptions made about the structure of silyl acetylene were the same as for CH_3NYZ. It was assumed that the silyl group had local C_{3v} symmetry and that the CCH-group was linear. The geometric parameters chosen to define the structure were the bonded distances SiH, SiC, CC, CH and the angles HSiC and SiCC. In any deviation of the latter angle from 180° the conformation of the CCH group was such that it was staggered with respect to the silyl protons. In the molecular model chosen for silyl trifluoromethylacetylene the assumptions made were that the silyl and trifluoromethyl groups had local C_{3v} symmetry and that the SiCCC skeleton was linear. The terminal groups were fixed in a staggered conformation. The geometric parameters chosen to define the structure were the bonded distances SiH, SiC, C≡C, C–C, CF and the angles CCF and CSiH.

Silyl Acetylene Refinement. For $SiH_3CC'H'$ satisfactory refinements were carried out on the SiH, SiC, CC' and C'H' bonded distances, the SiCC' angle and the amplitudes of vibration of the

SiC and CC' bonded and the Si...C' non-bonded atom pairs. The amplitude of vibration of the SiH bonded atom pair refined if the amplitudes of the SiC and CC' vibrations were fixed at their refined values. In addition, the three C...H amplitudes of vibration refined when they were made equal and tied to each other; the same was found for the three C'...H amplitudes of vibration. These constraints were necessary because of overlap of the C...H and C'...H distances with other distances in the radial distribution curve (Figure 6.7). Because of overlap of the C'H', SiH' and C..H' distances with other distances in the radial distribution curve the amplitudes of vibration of the C'H', SiH' and C...H' atom pairs were fixed at typical values.[124] The amplitudes of vibrations of all the H...H non-bonded distances were also fixed since they contributed little to the total scattering intensity. Attempts to refine the HSiC angle were unsuccessful; the angle tended to increase and so was fixed at a value which was slightly larger than the tetrahedral angle. The SiCC' angle refined to a value of $175.4 \pm 0.4^{\circ}$; this suggests that the SiCCH group is approximately linear. The Si-C and C≡C' distances found were 1.813Å and 1.221Å respectively and the Si...C' distance was 3.031Å; if the SiCCH fragment is truely linear this gives an Si...C' shrinkage of 0.003Å.

Table 6.6. Weighting Functions, Correlation Parameters and Scale Factors

Compound	Camera Height (mm)	ΔS	S_{min}	S_1	S_2	S_{max}	P/h	Scale Factor	Wavelength
SiH_3CCH	500	2	26	44	120	154	0.3942	0.660 ± 0.017	0.05659
SiH_3CCCF_3	250	4	64	80	250	300	0.3427	0.843 ± 0.025	0.05663
	500	2	28	37	140	154	0.4507	0.957 ± 0.020	0.05663

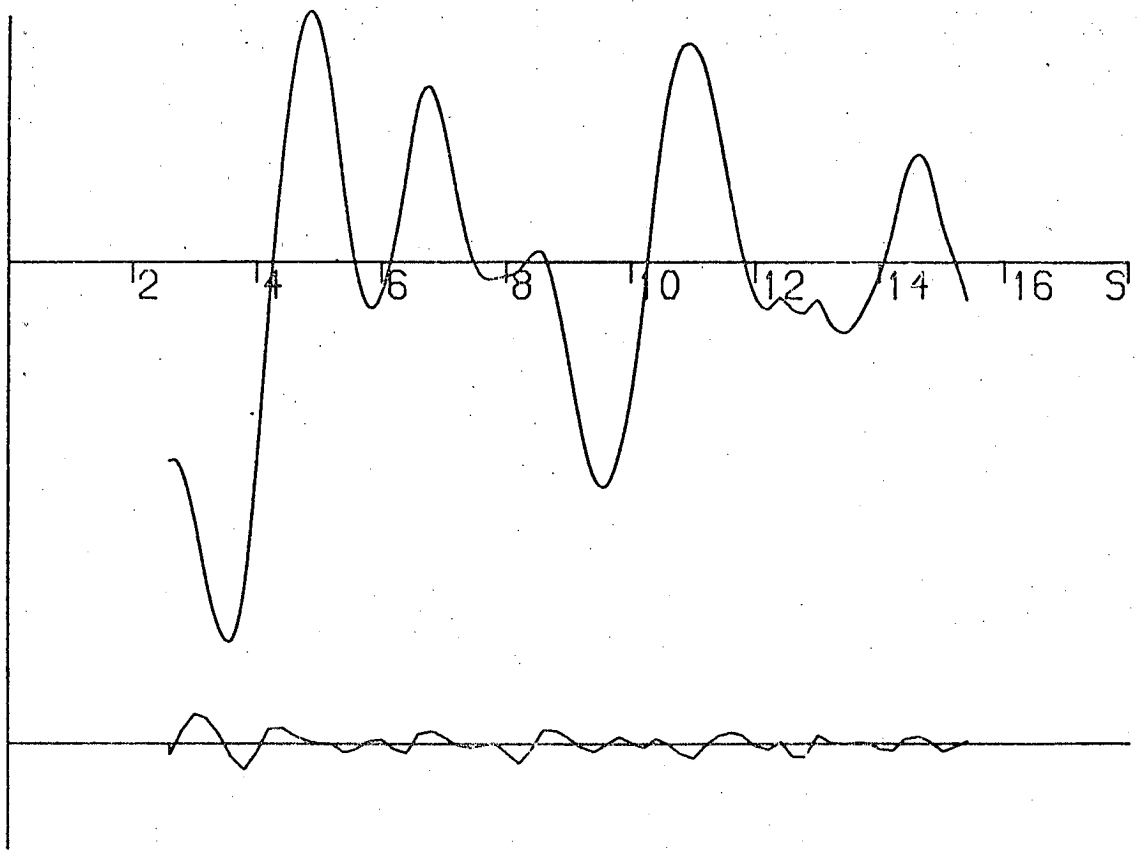


Fig. 6.5. Silyl acetylene intensity data.

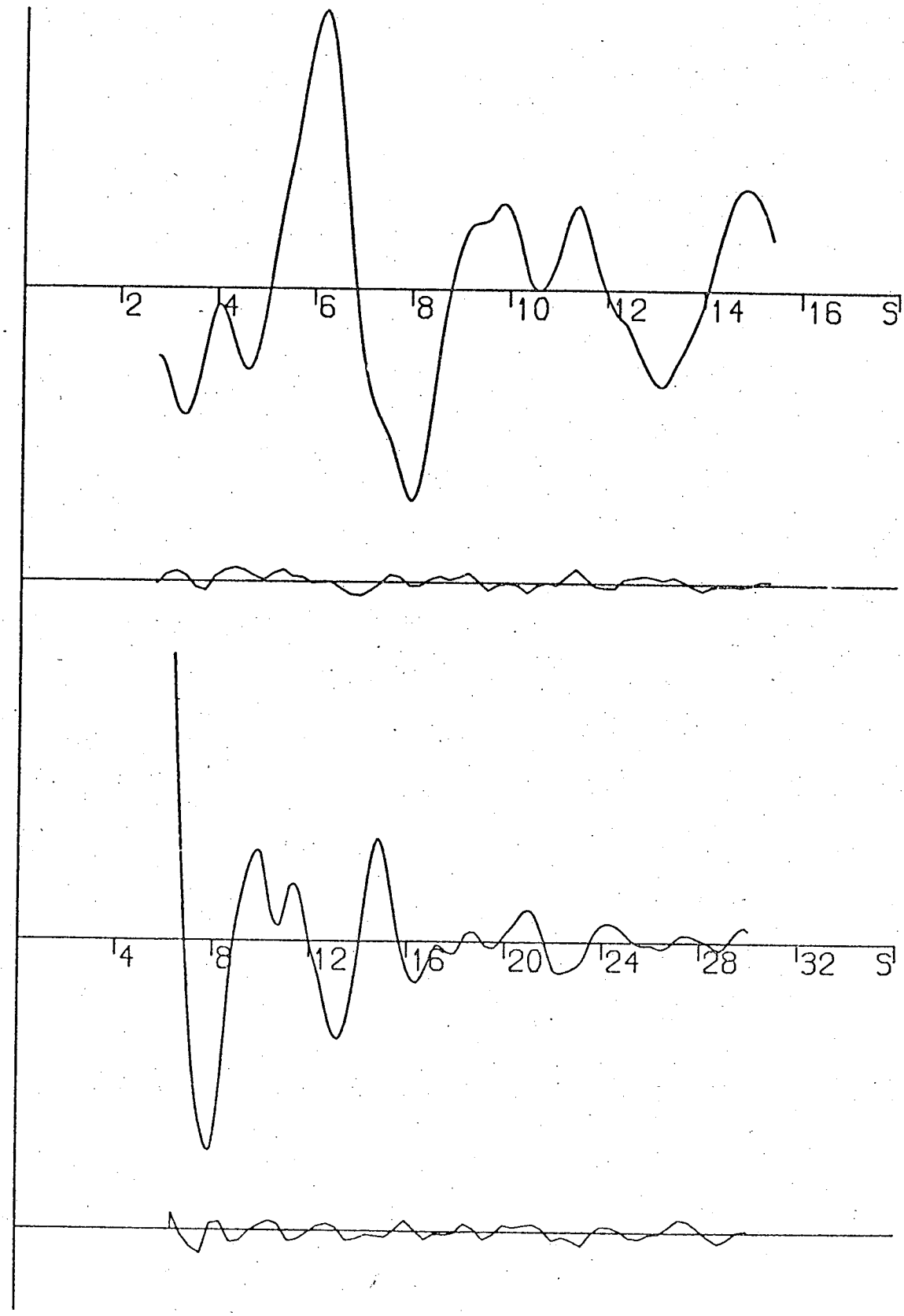


Fig. 6.6. Silyl Trifluoromethylacetylene intensity data.

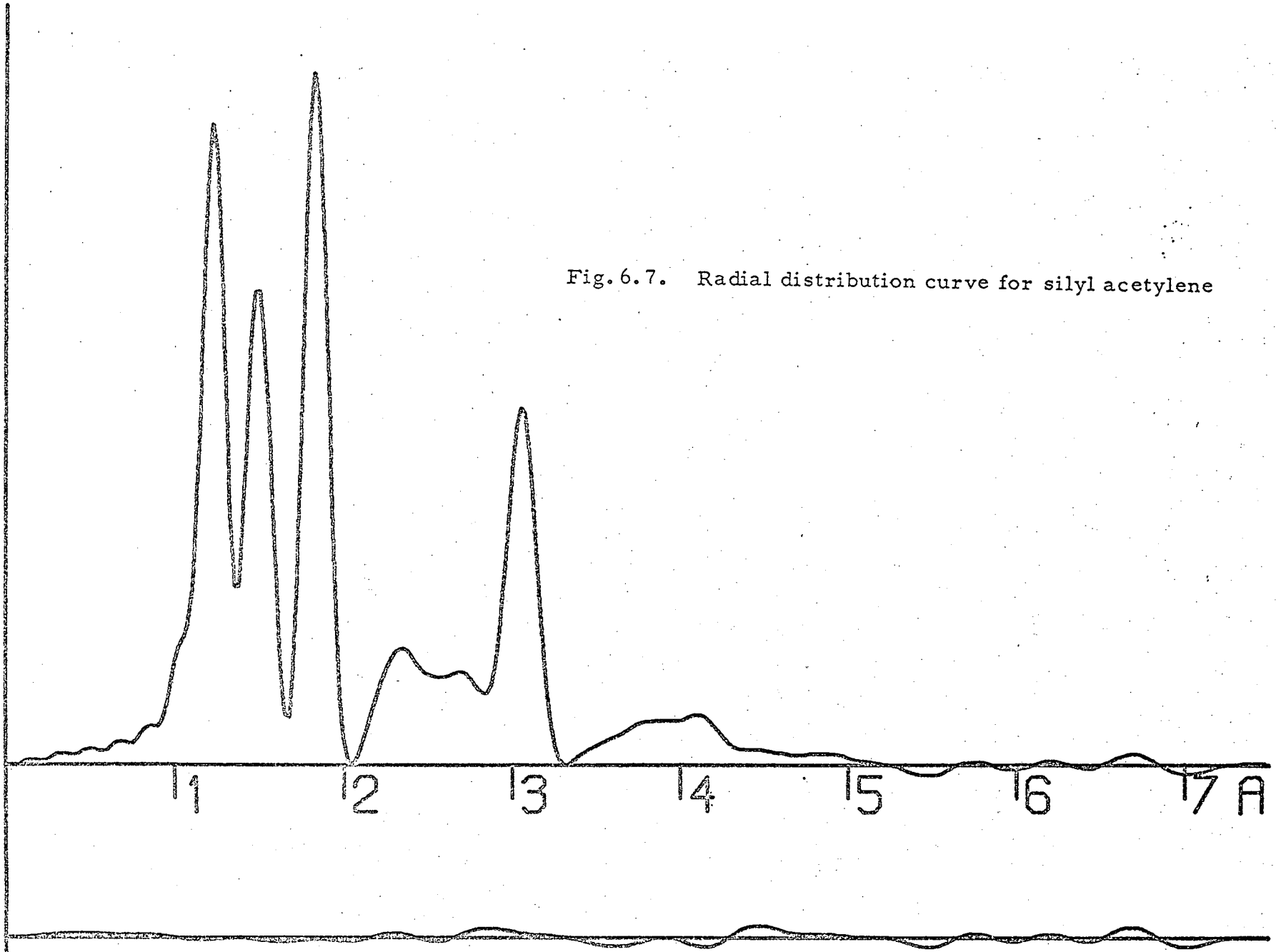


Fig. 6.7. Radial distribution curve for silyl acetylene

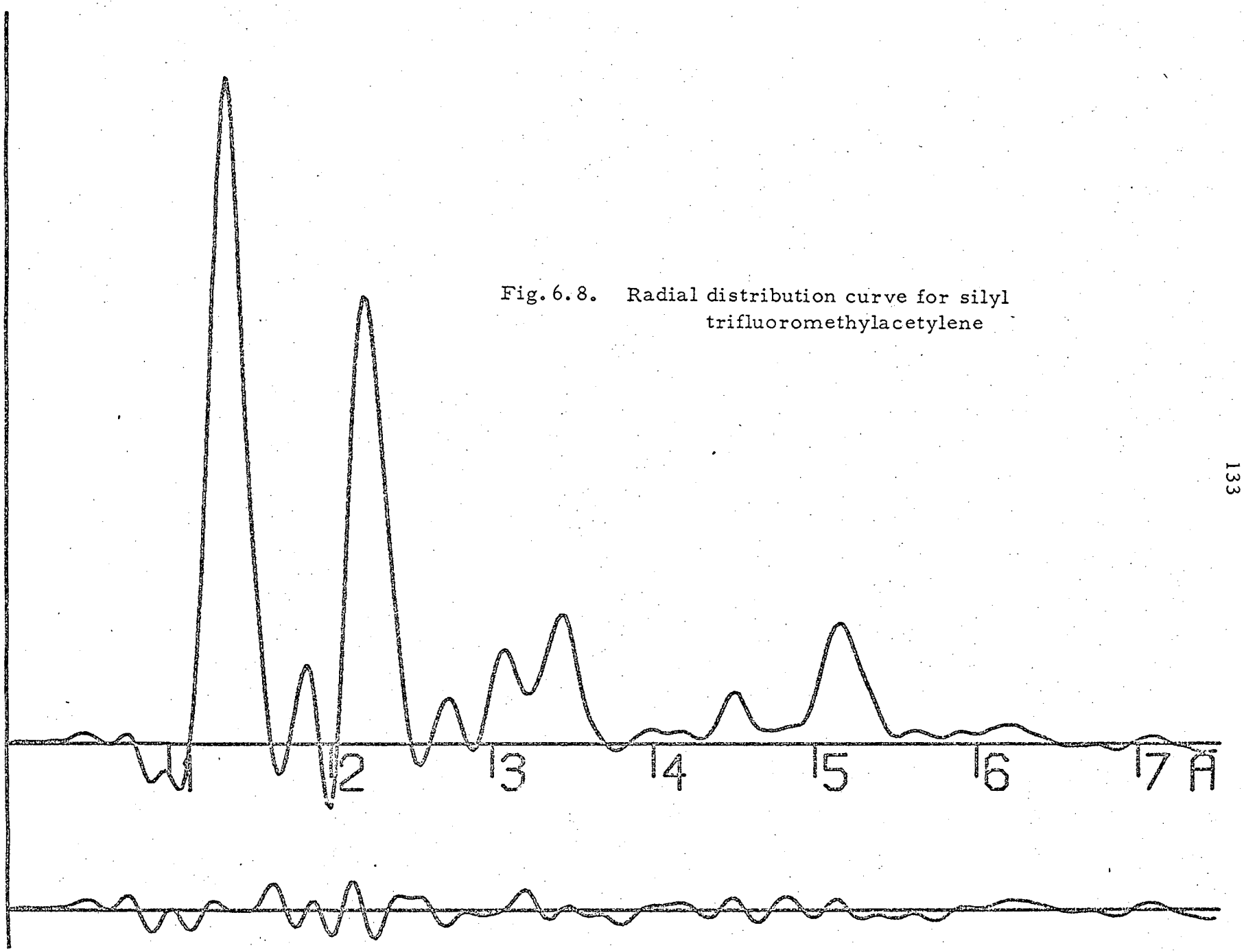


Fig. 6.8. Radial distribution curve for silyl trifluoromethylacetylene

Silyl Trifluoromethylacetylene Refinement. For $SiH_3CC'C''F_3$, satisfactory refinements were carried out on the SiC, CC', C'C" and C"F bonded distances, the CCF angle and the amplitudes of vibration of the FC" bonded and F...F, F...C, F...Si and Si...C' non-bonded atom pairs. In addition, because of overlap between the F...C' and F...F distances in the radial distribution curve (Figure 6.8), the F...C' amplitude would only refine with the F...F amplitude tied at a constant ratio to it. The other amplitudes of vibration would not refine either because of overlap of distances in the radial distribution curve or because of their small contribution to the total scattering intensity; they were fixed at typical values.[124]

Final parameters for the compounds and the least squares correlation matrices are given in Tables 6.7, 6.8, and 6.9. The lowest R factors were 0.12(SiH_3CCH) and 0.14(SiH_3CCCF_3).

The shortening of the Si-C bond from silyl cyanide to silyl acetylene found by microwave studies is confirmed. The value of 1.813Å found above however is 0.013Å shorter than that obtained by microwave spectroscopy. The reduction in r(Si-C) from silyl cyanide to silyl acetylene is found also in the microwave studies of the corresponding germyl compounds; r(Ge-C) is 1.919Å in germyl cyanide[127] and 1.896Å in germyl acetylene.[128] This effect may be related to the greater electronegativity of N than C; electron withdrawal by N may be strong enough to significantly

Table 6.7. Molecular Parameters for $SiH_3CC'H'$

A. Independent Distances

		Distance	Amplitude
r1	(Si-H)	1.483 ± 0.007	0.055 (fixed)
r2	(Si-C)	1.813 ± 0.004	0.052 ± 0.007
r3	(C-C')	1.221 ± 0.005	0.032 ± 0.021
r4	(C'-H')	1.075 ± 0.019	0.055 (fixed)

B. Dependent Distances

d5	(H...H)	2.410 ± 0.018	0.100 (fixed)
d6	(Si...H')	4.098 ± 0.033	0.090 (fixed)
d7	(Si...C')	3.031 ± 0.016	0.072 ± 0.012
d8	(C'...H)	3.842 ± 0.023	0.201 ± 0.046
d9	(C'...H)	3.789 ± 0.019	0.201 (tied to U8)
d10	(C'...H)	3.789 ± 0.019	0.201 (tied to U8)
d11	(H...H')	4.868 ± 0.032	0.160 (fixed)
d12	(H...H')	4.788 ± 0.029	0.160 (fixed)
d13	(H...H')	4.788 ± 0.029	0.160 (fixed)
d14	(C...H')	2.288 ± 0.024	0.075 (fixed)
d15	(C...H)	2.709 ± 0.012	0.162 ± 0.037
d16	(C...H)	2.709 ± 0.016	0.162 (tied to U15)
d17	(C...H)	2.709 ± 0.016	0.162 (tied to U15)

C. Independent Angles

1	(H-Si-C)	110.2 (fixed)
2	(Si-C-C)	$175.4^\circ \pm 0.6^\circ$

D. Dependent Angle

3	(H-Si-H)	$108.7^\circ \pm 0.2^\circ$

Table 6.8. Molecular Parameters for $SiH_3CC'C''F_3$

A. Independent Distances

		Distance	Amplitude
r1	(F-C'')	1.335 ± 0.002	0.047 ± 0.004
r2	(C''-C')	1.472 ± 0.011	0.045 (fixed)
r3	(C'-C)	1.207 ± 0.009	0.040 (fixed)
r4	(Si-C)	1.825 ± 0.006	0.070 (fixed)
r5	(Si-H)	1.500 (fixed)	0.060 (fixed)

B. Dependent Distances

d6	(F...F)	2.173 ± 0.007	0.082 ± 0.006
d7	(F...C')	2.302 ± 0.010	0.100 (fixed)
d8	(F...C)	3.379 ± 0.015	0.110 ± 0.010
d9	(F...Si)	5.120 ± 0.023	0.162 ± 0.009
d10	(F...H)	5.592 ± 0.023	0.150 (fixed)
d11	(F...H)	6.071 ± 0.025	0.150 (fixed)
d12	(C...C)	2.679 ± 0.017	0.048 (fixed)
d13	(C''...Si)	4.504 ± 0.022	0.138 (fixed)
d14	(C''...H)	5.192 ± 0.023	0.140 (fixed)
d15	(Si...C')	3.032 ± 0.013	0.066 ± 0.015
d16	(C'...H)	3.797 ± 0.015	0.130 (fixed)
d17	(C...H)	2.711 ± 0.009	0.100 (fixed)
d18	(H...H)	2.427 ± 0.006	0.100 (fixed)

C. Independent Angles

1	(C-C-F)	$110.1^\circ \pm 0.4^\circ$
2	(C-Si-H)	109.5° (fixed)

Table 6.9. Least Squares Correlation Matrices for a) SiH_3CCH and b) SiH_3CCCF_3, multiplied by 1000

a.

r1	r2	r3	r4	2	u2	u3	u7	u8	u15	k1
1000	744	660	178	-722	-141	-300	140	-20	167	-2
	1000	404	213	-676	-128	-205	92	-26	79	6
		1000	-135	-737	22	-420	127	107	142	51
			1000	-138	-258	541	-165	-332	-25	-399
				1000	69	255	-178	-119	-264	1
					1000	-130	340	83	132	542
						1000	-51	-201	-52	-17
							1000	-5	617	540
								1000	-58	142
									1000	189
										1000

b.

r1	r2	r3	r4	1	u1	u6	u8	u9	u15	k1	k2
1000	-27	199	122	-202	56	-110	-125	-125	-88	-274	-258
	1000	-269	376	-771	-365	-7	178	13	-3	265	349
		1000	-391	-232	322	307	-221	-183	-67	-424	-388
			1000	-298	-240	-189	-20	-44	-104	86	67
				1000	203	-245	-42	118	121	32	-68
					1000	275	-36	73	40	174	66
						1000	58	57	-8	226	169
							1000	89	168	225	238
								1000	67	277	271
									1000	164	78
										1000	439
											1000

reduce the electron density in the Si-C bond leading to a lengthening of the bond. The C-Si bond will have a small amount of (p-d)π bonding and if electron withdrawal from this component of the bond is mainly responsible for the bond lengthening then this may explain why the methyl analogues do not show the same effect in the CH_3-C bond. The value of r(Si-C) in SiH_3CCCF_3 is 1.825Å ; this lies between the values found for SiH_3CCH and SiH_3CN. Withdrawal of electrons by the CF_3 group may have the same effect on the Si-C bond as N had in SiH_3CN but to a lesser extent because of the greater distance over which the effect must be transmitted.

The value of r(C≡C) is also of interest. The triple bond in SiH_3CCH is slightly longer than the average value for these bonds (1.21Å)[129]; for SiH_3CCCF_3 this bond is considerably shorter (1.207Å) and is very similar in length to the triple bond in $HCCCF_3$(1.201Å).[130] Generally, substitution of electron-withdrawing species on acetylenic groups is known to strengthen the C≡C bond; for the compound HCCF, r(C≡C) is 1.198Å.[129]

The bond lengths within the CCF_3 group in $HCCCF_3$ agree well with those determined for SiH_3CCCF_3.

CHAPTER 7

SOME CONCLUSIONS AND SUGGESTIONS FOR FUTURE WORK

Throughout the work described in this thesis considerable use has been made of n.m.r. spectroscopy. It has been used both for characterisation of products and as a means of obtaining more detailed information about the environments of nuclei within the complexes. Towards both these ends heteronuclear double resonance has been extensively used. The determination of $\delta(^{195}Pt)$ has, for example, enabled the components of a mixture of six-coordinated monohydride complexes of platinum to be identified; this would have been almost impossible from the simple ^{1}H n.m.r. spectrum because of the similarities of the proton resonances. In other cases $\delta(^{195}Pt)$ was used to confirm the assignments made from other techniques. Over the range of platinum silicon complexes studied, the chemical shift of platinum varied by relatively small amounts, although in most cases they were significant enough to be useful. If it had been possible to observe the ^{29}Si spectrum (by double resonance techniques) of those complexes, other useful parameters such as $\delta(^{29}Si)$ and $J(^{29}SiX)$ could have been obtained. However, to use this technique the ^{29}Si satellites of the main Si<u>H</u> resonance have to be visible in the ^{1}H n.m.r. spectrum; this requires relatively large concentrations of complex in solution and in many cases this could lead to problems with solubility. From a more theoretical viewpoint, double resonance techniques have been used to study variations in the environments of nuclei (esp. Pt and P) over a range of complexes. This has not been considered in

detail in this thesis but the area is one which should provide fruitful research in future. The factors which determine the chemical shifts of heavy nuclei are complex and not well understood. However, with the information which is being amassed from double resonance experiments on complexes of platinum and other heavy nuclei, it may be possible to gain an insight into this problem. For this purpose a much wider range of ligands than those discussed in this work would have to be considered.

With improvements in n.m.r. spectrometers, the direct observations of the resonances of nuclei other than ^{1}H and ^{19}F has become a routine procedure. In future more use could be made of this in distinguishing products. Because of the 100% abundance of ^{31}P, phosphorus spectra should prove quite valuable for this purpose. Also accurate values of $^{1}J(Pt-P)$ could be used, keeping in mind the assumptions made,[19,20] to gain more detailed information about the cis and trans influences of other ligands in the complexes. It may also be possible to study the platinum-silicon complexes by ^{29}Si n.m.r. For example, the products from the reaction of Si_3H_8 with trans-$[PtHI(PEt_3)_2]$ should be identified quite readily by this technique. Also, since silicon is directly involved in the intermolecular migration of the cyclopentadienyl derivatives of silane and the platinum silyl complexes, more detailed information should be obtained about this process.

The study of the six-coordinated hydride complexes of platinum, $PtH_2XY(PEt_3)_2$ and $PtHXY_2(PEt_3)_2$ (X, Y = halogen), is almost complete. The products have been characterised by their n.m.r. parameters and two also by infrared spectroscopy and C, H analysis. The mechanism of reaction has also been determined. The mode of addition of HX to trans-$[PtHY(PEt_3)_2]$ was not established conclusively since the initial product from the addition reaction underwent very rapid 'scrambling' of halogens or protons. If the halogens were 'scrambling', a process which would be facilitated by the strong trans effect of the hydride ligands, then use of a ligand which formed a stronger bond with platinum (eg. -CN) might stabilise the product enough to allow it to be observed. The range of compounds used as HX could be extended; preliminary studies have been made with X = CN, SH, SeH. However, perhaps a more interesting possibility is that, by forming a dihydride complex - $PtH_2XY(PEt_3)_2$ - then allowing hydrogen to be evolved, platinum complexes, which by other routes might be difficult to obtain, could be prepared.

The reaction of silyl halides with platinum complexes of the type trans-$[PtHX(PEt_3)_2]$ and trans-$[PtX_2(PEt_3)_2]$ is now well characterised; the mechanism of oxidative addition of Si-H across platinum followed by elimination of two ligands has been proven both by the products obtained and the six-coordinated intermediates observed. It is of interest that, even with an active group bound

to silicon, the reaction pathway still favours the formation of a Pt-Si bond. Possibly the lack of reaction of the acetylenic groups in SiH_3CCH and SiH_3CCCF_3 with the platinum group is due to a kinetic barrier. The Si-H addition-elimination reaction is almost complete within a few hours at room temperature whereas, for example, the reaction of F_3CCCCF_3 with trans-$[PtClH(PEt_3)_2]$ requires heating to 363K for 25 hr. to give a 41% yield of $PtCl[CF_3.CC(CF_3)H](PEt_3)_2$.[131] All the complexes studied in this work have been mono-silyl complexes of platinum. The compound cis-$[PtH(SiR_3)(PPh_3)_2]$[132] is known; reaction of this with SiH_3X might produce a product of the form cis or trans-$[Pt(SiH_2X)SiR_3(PPh_3)_2]$. Complexes of this type could provide interesting samples for ^{29}Si n.m.r. studies.

An extension to the study of the chemistry of platinum could be made in the area of complexes containing the Pt-M bond (M = Sn, Se or Te); trans-$[PtH(SeH)(PPh_3)_2]$ is known[133] and has been characterised by ^1H n.m.r. spectroscopy. Sn, Se and Te all have isotopes with $I = \frac{1}{2}$ with natural abundances of approximately 8%; if these compounds could be prepared some very interesting n.m.r. work would result.

The instability of the palladium-silicon complexes meant that they could only be studied by n.m.r. spectroscopy. A full characterisation of the products was not possible and they were identified by analogy with the corresponding platinum system. It

does appear that, although no six-coordinated intermediate was observed, these complexes are formed by an addition-elimination mechanism.

CHAPTER 8

EXPERIMENTAL

Experimental

8.1. General Experimental Methods

All volatile compounds were handled in a conventional pyrex glass vacuum system with greased taps. Quantities of condensible materials were measured in calibrated volumes using a glass spiral gauge to measure pressures. Volumes of non-condensible gases were measured using a Toepler pump. Involatile air-sensitive solids were handled under dry oxygen-free nitrogen in a dry bag. Reactions were carried out either in greaseless tap ampoules or in sealed n.m.r. tubes. Volatile compounds were purified by trap to trap distillation and their purity checked by their i.r. and n.m.r. spectra.

Instruments.

Low resolution infrared spectra were recorded using a Perkin-Elmer 457 spectrometer (range 4000 - 250 cm^{-1}) and for high resolution spectra a Perkin-Elmer 225 grating spectrometer (range 5000 - 200 cm^{-1}) was used. Vapour phase and solution spectra were recorded in the normal manner. Nujol mulls of moisture sensitive compounds were recorded using CsI plates held in a sealed container. The nujol was dried over molecular sieve. Raman spectra were recorded on a Cary 83 spectrometer using argon ion laser excitation at 4880$\AA$ using powdered solid samples. Nuclear resonance spectra were recorded on a Varian Associates

HA100 spectrometer operating at 100 MHz(^{1}H) or 94.075(^{19}F). A more detailed account of the n.m.r. techniques employed is given in the following section. Mass spectra were obtained at various ionising voltages on an A.E.I. M.S.909 spectrometer.

Gas chromatography was done on a Pye 104 chromatograph using at column of 25% polyethylene glycol adipate on 60-72 mesh Diatomite. The column was maintained at 353K.

Analysis for C and H were carried out using a Perkin-Elmer 240 Elemental Analyser. Moisture sensitive compounds were sealed in aluminium pans under an atmosphere of nitrogen.

The instruments used to obtain electron diffraction data are described in Section 8.3.

8.3. N.M.R. and double resonance techniques

For proton n.m.r. spectra the spectrometer was used in its HA mode operating at 100 MHz. Using the normal field or frequency mode the spectrometer had a range of 2000 Hz to high frequency and 1000 Hz to low frequency of the lock signal. The overall range of the spectrometer, obtained by using the field or frequency mode of operation in conjunction with locking on the first lower or higher frequency sideband of the main lock resonance, was 2000 Hz on either side of the lock signal. This meant that, using tetramethylsilane as lock, the low frequency limit of the instrument was 3OT and so the only resonances which could not be observed

were the low frequency ^{195}Pt satellites of some hydride complexes.

The probe of this instrument was double tuned to accept a second radiofrequency, provided by a Schlumberger FS 30 frequency synthesizer.[134] This instrument was used for all the heteronuclear double resonance experiments. No phase locking system was used but the relative frequencies of the independent crystal sources of the spectrometer and synthesizer were checked after each experiment so that measured irradiation frequencies should be correct to at least one part in 10^7. The technique employed to obtain the decoupling frequency was as follows. With the instrument operating on frequency sweep the chart recorder pen on the spectrometer was positioned on the peak in the spectrum which was to be 'collapsed'. The second radiofrequency was then varied until the pen dropped towards the baseline. By reducing the power of the decoupling frequency more selective 'tickling' experiments could be done. As mentioned in section 1.1 corrections had to be applied to this observed decoupling frequency. These frequencies are normally reported under conditions such that tetramethylsilane would resonate at exactly 100 Mc.s.$^{-1}$. To do this the following corrections, scaled down from 100 MHz for the frequency under consideration, have to be applied.

a) If TMS is not used as lock, the observed frequency has to be corrected by an amount equal to ν(TMS) - ν(lock).

b) The instrument locks on to a 2500 c/s modulation of the main TMS resonance. Therefore, in order that the observed frequency is measured relative to the TMS centreband, a correction of $2500 \pm x$ c.s.$^{-1}$ (where x = any additional offset in the instrument) is also applied.

c) Finally the radiofrequency produced by the crystal source in the instrument deviates slightly from 100 MHz; the exact value of this is measured and the observed frequency corrected for by this amount.

The signs of corrections (a) and (c) were always positive. For (b), the sign was positive if the instrument was locked on to the low frequency sideband of the main lock resonance and vice versa.

For homonuclear double resonance experiments sidebands of the spectrometer frequency, generated by a Muirhead decade oscillator, were used.

^{19}F n.m.r. spectra were first observed using the instrument in its HR mode of operation. In suitable cases, the resonance was also observed using the HA mode; the first 2500 c/s sideband of the arcton resonance was used as a lock signal.

8.4. Electron Diffraction Techniques

Electron diffraction scattering data for each species were

obtained in the form of photographic plates using the Balzers' KD.62 instrument at the University of Manchester Institute of Science and Technology.[135] The photographic intensities were reduced to digital form using a fully automated Joyce-Loebl microdensitometer at the Royal Observatory, Edinburgh. Reduction of the data and least squares refinements were performed on an IBM 360/50 computer at the Edinburgh Regional Computing Centre.

The programmes used are in four stages. The first stage combines the corrected traces and subtracts a calculated atomic scattering curve. A cubic curve, found by least-squares fitting, is then subtracted to level the data across the plate. The next stage allows the subtraction of a background curve to account for incoherent atomic and other extraneous scatterings. The best curve was found, in each case, by comparison of data from all the plates. Further, relatively minor, adjustments could be made to the background later. The third stage used a least squares refinement programme based on that of Hedberg.[136] The scattering factors of Cox and Bonham[137] were used. Quoted errors were increased to allow for systematic errors such as in the measurement of the wavelength. This is normally obtained from the diffraction of powdered thallous chloride and by direct measurement of the high voltage supply used. The estimated error in the wavelength was usually $\pm$ 0.00003 Å. Two 'R factors' are also calculated by this

programme,

$$R_G = . (\bar{U}WU/\bar{I}WI)^{\frac{1}{2}}$$

$$R_D = (\Sigma w_{jj} U^2_j / \Sigma w_{jj} I^2_j)^{\frac{1}{2}}$$

where I is the vector of intensities, U the vector of residuals and W the weight matrix with elements w_{jk}. The final stage of the programmes calculates and plots the radial distribution curves [P(r) and P(r)/r] by Fourier inversion of the intensity curves. The distances calculated in the refinement stage correspond to the centres of gravity of the peaks in the P(r)/r curve.[138]

8.4. Preparation of Starting Materials

Compound	Method	Reference
SiH_4	$SiCl_4 + LiAlH_4$	139
SiH_3Br	$PhSiCl_3 + LiAlH_4$ then HBr	140
SiH_3Cl	$SiH_3Br + HgCl_2$ (streaming)	141
SiH_3I	$(SiH_3)_3N + HI$	142
SiH_3F	$(SiH_3)_3N + NH_4HF_2$	143
SiH_3CN	$SiH_3Br + AgCN$ (streaming)	-
SiH_3CCH	$SiH_3Br + NaCCH$	-
GeH_4	$GeO_2 + BH_4^-$	144
GeH_3Br	$GeH_4 + HBr + AlBr_3$	145
GeH_3Cl	$GeH_3Br + HgCl_2$ (streaming)	-

$HCCCF_3$	$Cl_2C{:}CCl.CF_3 + Zn$ then H_2O	146
HI	$HI(aq) + P_2O_5$	-
DCl	$PCl_5 + D_2O$	-
DBr	$PBr_5 + D_2O$	-
DI	$P(red) + I_2 + D_2O$	-
CH_3N_3	$(Me)_2SO_4 + NaN_3$	147

For the following L = Et_3P and X = halogen.

c- and t-$[PtCl_2L_2]$	$K_2PtCl_4 + L$	148
t-$[PtX_2L_2]$	NaX + t-$[PtCl_2L_2]$	149
t-$[PtClHL_2]$	N_2H_4 + c-$[PtCl_2L_2]$	150
t-$[PtHXL_2]$	NaX + t-$[PtClHL_2]$	150
t-$[PtX_4L_2]$	X_2 + t-$[PtX_2L_2]$ ($X \neq I$)	151
t-$[Pt(CH_3)IL_2]$	$MeMgI$ + t-$[PtCl_2L_2]$	91
c-$[Pt(CH_3)_2L_2]$	$MeLi$ + c-$[PtCl_2L_2]$	91
t-$[Pt(MHXY)ZL_2]$	MH_2XY + t-$[PtHZL_2]$	29
c-t-$[PtH(SiH_2Y)X_2L_2]$	SiH_3Y + t-$[PtX_2L_2]$	29
t-$[Pt(CCH)_2L_2]$	$NaCCH$ + c-$[PtCl_2L_2]$	92
t-$[Pt(CCPh)_2L_2]$	$NaCCPh$ + c-$[PtCl_2L_2]$	92
t-$[Pt(CCCF_3)_2L_2]$	$IMg(CCCF_3)$ + t-$[PtCl_2L_2]$	152
c-and t-$[PdCl_2L_2]$	$K_2PdCl_4 + L$	153
t-$[PdX_2L_2]$	NaX + t-$[PdCl_2L_2]$	-

Si_3H_8, $SiH_3C_5H_5$ and $GeH_3C_5H_5$ were kindly supplied by Dr. J.E. Bentham. Other compounds were commercial products. Purities were checked spectroscopically. Melting points of solids and vapour pressures (where necessary) of volatile compounds were also checked.

Solvents were purified as follows:

Benzene	Analar grade, dried over sodium wire and distilled.
Toluene	As for benzene.
Tetramethylsilane	Distilled and found adequately pure.
Deuterobenzene	As for tetramethylsilane.
Methylene Chloride	Distilled from molecular sieve.
Chloroform	Shaken with activated alumina then distilled.
Diethyl ether	Dried over sodium wire.
Monoglyme	Shaken with potassium and anthracene until blue colour formed, then distilled.
Diglyme	As for monoglyme.
Ammonia	Warmed to 209K with sodium then distilled.
Dimethylformamide	Dried over molecular sieve.

8.5. Details of experiments

Exp. 2.1. Preparation of cis-trans-$[PtH_2XY(PEt_3)_2]$ (X, Y = halogen).

In a typical experiment (X = Y = Cl) trans-$[PtClH(PEt_3)_2]$ (0.832g, 0.18 mmol) was dissolved in methylene chloride containing

10% tetramethylsilane (ca. 3 ml.) and HCl (0.18 mmol.) was condensed in at 77K. The reagents were allowed to mix at 253K. For ^{1}H n.m.r. experiments when X ≠ Y, the reagents were allowed to mix at 183K and the spectrum was recorded initially at that temperature.

The complexes cis-cis-trans-$[PtCl_2H_2(PEt_3)_2]$ (Found: C, 28.75; H, 6.6%. $C_{12}H_{32}Cl_2P_2Pt$ requires C, 28.6; H, 6.4%) and cis-cis-trans-$[PtBr_2H_2(PEt_3)_2]$ (Found: C, 24.25; H, 5.45%. $C_{12}H_{32}Br_2P_2Pt$ requires C, 24.3; H, 5.45%) were isolated by removal of the solvent under reduced pressure at 253K.

Expt. 2.2. Preparation of cis/trans-trans-$[PtHXY_2(PEt_3)_2]$.

In a typical reaction (X = Y = I) trans-$[PtI_2(PEt_3)_2]$ (0.133g, 0.19 mmol.) was completely dissolved in methylene chloride containing 10% tetramethylsilane and HI (0.19 mmol.) was condensed in at 77K. The reagents were allowed to mix at 253K when an immediate reaction took place. The temperatures at which the reagents were mixed varied. For X = Y = Cl, Br 253K was adequate, but for X ≠ Y the reagents were mixed at 183K in order to detect the first products formed.

Expt. 2.3. Reaction of X_2 with trans-$[PtHY(PEt_3)_2]$

In a typical reaction (X = Y = Cl) trans-$[PtClH(PEt_3)_2]$ (0.092g, 0.20 mmol.) was dissolved in methylene chloride containing 10% tetramethylsilane and Cl_2 (0.20 mmol.) was

condensed in at 77K. The reactants were allowed to mix at 183K and the ^{1}H n.m.r. spectrum was recorded initially at this temperature. A similar technique was used for the reaction of XY with trans-$[PtHZ(PEt_3)_2]$ (X, Y, Z = halogen).

Expt. 3.1. Reaction of SiH_3CCH with trans-$[PtClH(PEt_3)_2]$

SiH_3CCH (0.22 mmol.) was allowed to react with trans-$[PtClH(PEt_3)_2]$ (0.105g, 0.22 mmol.) in benzene (ca. 3 ml.) at room temperature. Hydrogen was evolved - 0.170 mmol. (1.5 hr.), 0.195 mmol. (15 hr.), 0.220 mmol. (30 hr.) - and the colourless solution was found to have turned pale yellow after 15 hr. On evaporation of the solvent at 251K, trans-$[PtCl(SiH_2CCH)(PEt_3)_2]$ was obtained as pale yellow crystals. (Found: C, 31.1; H, 6.13%. $C_{14}H_{33}ClP_2PtSi$ requires C, 32.2; H, 6.33%). In the infrared spectrum (nujol mull) peaks were observed at 3285 m (νCH), 2095 s(νSiH), 2015 m (νCC), 975 s (δSiH), 822 vs (δSiH), 665 w, 631 m, 585 m, 465 w, 415 m, 385 ms, 300 w (νPtSi), 283 w (νPtCl)cm^{-1}.

Solutions of trans-$[PtI(SiH_2CCH)(PEt_3)_2]$ and trans-$[PtCl(SiH_2CCCF_3)(PEt_3)_2]$ were obtained similarly; these products were identified by their n.m.r. parameters.

Expt. 3.2. Reaction of SiH_3CCCF_3 with trans-$[PtI_2(PEt_3)_2]$

Trans-$[PtI_2(PEt_3)_2]$ (0.137g, 0.20 mmol.) was treated with SiH_3CCCF_3 (0.20 mmol) in benzene containing 10% tetramethylsilane (ca. 3 ml.) at 273K. Evaporation of the solvent at 251K gave pale

yellow crystals of trans-$[PtHI_2(SiH_2CCCF_3)(PEt_3)_2]$ (Found: C, 22.45; H, 4.25%. $C_{15}H_{33}F_3I_2P_2PtSi$ requires C, 22.3; H, 4.08%). In the infrared spectrum (nujol mull) peaks were observed at 2230 s (νPtH), 2205 s (νSiH), 2194 s (νSiH), 2179 s (νCC), 1401 m, 1252 vs, 1212 s, and 1138 vs (νCF), 953 m, 810 s (δPtH), 674 m, 635 m, 622 w, 588 m (ρSiH), 332 w (νPtSi) cm^{-1}.

Reaction of SiH_3CCH with trans-$[PtI_2(PEt_3)_2]$ was carried out in a similar way. Evaporation of the solvent at 251K gave pale yellow crystals of trans-$[PtHI_2(SiH_2CCH)(PEt_3)_2]$ (Found: C, 21.88; H, 4.23%. $C_{14}H_{34}I_2P_2PtSi$ requires C, 22.69; H, 4.59%). These crystals however proved too unstable for a satisfactory infrared spectrum to be obtained, though infrared peaks were observed at 2220 mw, 2198 ms and 2015 m cm^{-1} before decomposition spoilt the quality of the spectrum.

Expt. 3.3. Reaction of $GeH_3C_5H_5$ with trans-$[PtHI(PEt_3)_2]$

$GeH_3C_5H_5$ (0.17 mmol.) was allowed to react with trans-$[PtHI(PEt_3)_2]$ (0.095g, 0.17 mmol.) at 263K in fluorotrichloromethane for 1.5 hr. On evaporation of the solvent at 258K, trans-$[Pt(GeH_2C_5H_5)I(PEt_3)_2]$ was obtained as a yellow solid. (Found: C, 28.56; H, 5.32%. $C_{17}H_{37}GeIP_2Pt$ requires C, 29.25; H, 5.34%). In the infrared spectrum (nujol mull) peaks were observed at 1997 s, 1984 s; 1952 sh and 1940 s (νGeH), 1418 m, 1292 w, 1253 m, 1238 m, 1220 m, 1155 br. m., 1084 m, 1034 s, 1008 m, 993w, 988 w,

925 (s) (δGeH), 883 s (δGeH), 826 m, 791 s, 764 s, 745 m, 722 m, 660 s, 634 m, 548 m, 534 m, 478 w ; 415 m and 382 w (νPtP); 351 s, 330 w, 261 w cm^{-1}.

Solutions of trans-$[PtI(SiH_2C_5H_5)(PEt_3)_2]$, trans-$[PtCl(SiH_2C_5H_5)(PEt_3)_2]$ and trans-$[PtCl(GeH_3C_5H_5)(PEt_3)_2]$ were prepared similarly.

Expt. 3.4. Reaction of SiH_3CN with trans-$[Pt(CN)H(PEt_3)_2]$

Treatment of trans-$[Pt(CN)H(PEt_3)_2]$ (0.086g, 0.19 mmol.) with SiH_3CN (0.19 mmol) in methylene chloride at room temperature for 0.5 hr. gave a clear solution. On evaporation of the solvent at 243K trans-$[Pt(CN)SiH_2CN(PEt_3)_2]$ was obtained as an off-white solid (Found: C, 32.90; H, 6.73%. $C_{14}H_{32}N_2P_2PtSi$ requires C, 32.74; H, 6.29%). Slow decomposition of this solid reduced the quality of the infrared spectrum. The following infrared peaks (nujol mull) were observed; 2175 m, 2138 s, 2112 s; and 2070 m (νSiH and νCN), 1415 m, 1260 m, 1037 s, 1002 w, 978 w, 952 w, 830 m, 768 s, 736 m, 698 m, 634 m, 489 w, 391 w, 348 w, 274 w cm^{-1}.

In the same way solutions of trans-$[Pt(MH_2X)Y(PEt_3)_2]$ (M = Si or Ge; X = H, Cl, CN; Y = Cl, CN) were prepared. Evaporation of the solvent at 250K from a solution of trans-$[Pt(CN)GeH_3(PEt_3)_2]$ in benzene gave a yellow powder (Found: C, 29.83; H, 6.09%. $C_{13}H_{33}GeNP_2Pt$ requires C, 29.29; H, 6.24%).

In the infrared spectrum (nujol mull) peaks were observed at 2115 m (νCN), 1965 br.s. (νGeH), 1424 m and 1414 m (δCH), 1253 w and 1239 w (νCC), 1038 s, 1051 m; 909 w, 893 m and 832 s (δGeH), 769 s, 732 s, 640 m (δCN), 545 (ρGeH), 478 w; 421 m and 394 m (νPtP), 246 w (νPtGe) cm^{-1}.

Expt. 3.5. Reaction of Si_3H_8 with trans-$[PtHI(PEt_3)_2]$

These reactions were carried out using the same technique as in Expt. 3.4. Benzene containing 10% tetramethylsilane was used as solvent and the reactants were allowed to mix at 273K. The volume of hydrogen evolved was measured, for different proportions of starting materials, using a Toepler pump. When a threefold excess of $PtHI(PEt_3)_2$ was used the following volumes of hydrogen were evolved; after 6 hr. at 273K 0.29 mmol of hydrogen was obtained from 0.13 mmol. of Si_3H_8 while after 12 hr. 0.30 mmol. had been evolved. By this time the solution was deeply coloured and effervescence had ceased. The possible products are discussed in Chapter 3.

Expt. 3.6. Reaction of Silyl and germyl halides with trans-$[Pt(CCX)_2(PEt_3)_2]$ (X = H, Ph, CF_3).

These reactions were studied with both equimolar proportions of reactants and a twofold excess of the silyl or germyl halide. In a typical experiment SiH_3Br (0.11 mmol.) was allowed

to mix with trans-$[Pt(CCPh)_2(PEt_3)_2]$ (0.070g. 0.11 mmol.) in deuterobenzene containing 10% tetramethylsilane (ca. 3 ml.). The reaction was followed by ^1H n.m.r. spectroscopy. These reactions were very slow and so the mixtures were heated to approximately 323K for several days. As discussed in Chapter 3 there was little or no reaction in many cases.

Expt. 3.7. Reaction of SiH_3I with trans-$[Pt(CH_3)I(PEt_3)_2]$

The technique used for this reaction was similar to those described above. On mixing SiH_3I (0.19 mmol.) with an equimolar quantity of $Pt(CH_3)I(PEt_3)_2$ at room temperature in benzene very rapid effervescence took place. The reaction was complete within five minutes and the products formed, mainly CH_3SiH_2I and trans-$[PtI(SiH_2I)(PEt_3)_2]$, were identified by ^1H n.m.r. spectroscopy. The non-condensible gas evolved was identified as methane from its infrared spectrum.

Expt. 4.1. Reaction of Silyl and germyl halides with trans-$[PdX_2(PEt_3)_2]$ (X = halogen).

These reactions were analogous to the one described in Expt. 3.1. In all cases equimolar quantities of reactants were allowed to mix at room temperature in benzene or deuterobenzene containing 10% tetramethylsilane (ca. 3 ml.) in a sealed n.m.r. tube. The reaction products were not stable enough to allow characterisation by

infrared spectroscopy or analysis for C, H. In a typical experiment SiH_3Cl (0.20 mmol.) was condensed onto trans-$[PdCl_2(PEt_3)_2]$ (0.081g, 0.20 mmol) in benzene/tetramethylsilane at 77K. These were allowed to mix at room temperature and the ^1H n.m.r. spectrum studied immediately and then at regular intervals up to three days. The products SiH_4, SiH_2Cl_2, trans-$[PdCl(SiH_2Cl)(PEt_3)_2]$ and trans-$[PdCl(SiHCl_2)(PEt_3)_2]$ were observed, the latter being the major product after several days.

Expt. 5.1. Preparation of SiH_3CCCF_3

$HCCCF_3$ was prepared by the method described by Finnegan and Norris.[146]

MeMgI was prepared by the action of MeI (0.425g) on magnesium turnings (0.075g) in refluxing sodium-dried diethyl ether in a sealed flask for two hours. $HCCCF_3$ (3.5 mmol.-excess) was condensed onto this solution at 77K and then these were allowed to mix at room temperature for two hours. The solution of $IMg(CCF_3)$ in ether was cooled to 77K and the methane pumped off. To facilitate purification of the final product the solvent was changed to diglyme at this stage. This was done by first condensing the diglyme into the reaction vessel then pumping off the ether. Because of the involatility of diglyme at room temperature the solution could be pumped on for about 0.25 hr. thus ensuring the removal of all the diethyl ether. SiH_3Br (2.8 mmol.) was then condensed onto the

solution and the reactants left at room temperature for O.5 hr. During this time there was effervescence and the formation of MgBrI as a precipitate.

The product was purified by trap to trap condensation. The main impurity was SiH_4 and this could be removed by fractionation through a trap held at 153K; SiH_3CCCF_3 was retained at this temperature.

GeH_3CCCF_3 was prepared by a similar technique. GeH_3Cl was used instead of the bromide since the reaction was found to be faster. The product was retained at 177K and so could be separated easily from GeH_4. Ge_2H_6 was also formed in the reaction and was more difficult to remove. Since Ge_2H_6 was slightly more volatile, repeated fractionation through 177K left a fairly pure sample of GeH_3CCCF_3.

Charactersiation of these products has been discussed in Chapter 5. The data obtained from vapour pressure measurements over a range of temperatures is given in Table 8.1.

Table 8.1. Vapour Pressure Data for MH_3CCCF_3 (M = Si, Ge)

a) SiH_3CCCF_3

Temperature (K)	Pressure (cm)
190.5	0.40
223.0	0.45
210.5	1.75
231.5	7.50
246.0	16.0
253.0	22.0

b) GeH_3CCCF_3

Temperature (K)	Pressure (cm)
213.0	0.33
224.0	0.83
231.5	1.58
242.0	3.38
242.5	3.42
253.0	6.80
253.5	7.10

References

1. W. McFarlane, Quarterly Rev., 1969, 23, 187.
2. F. Bloch, Phys.Rev., 1946, 70, 460.
3. F. Calderazzo, E.A.C. Lucken, D.F. Williams, J.Chem. Soc.(A), 1967, 154.
4. G.M. Bancroft, H.C. Clark, R.G. Kidd, A.T. Rake, H.G. Spinney, Inorg.Chem., 1973, 12, 728.
5. J.S. Griffith, L.E. Orgel, Trans.Far.Soc., 1957, 53, 601.
6. E.A.C. Lucken, K. Noack, D.F. Williams, J.Chem.Soc.(A), 1967, 148.
7. A. Pidcock, R.E. Richards, L.M. Venanzi, J.Chem.Soc.(A), 1968, 1970.
8. A.V. Zelewsky, Helv.Chim. Acta, 1968, 51, 803.
9. R.E. Dessy, T.J. Flautt, H.H. Jaffe, G.F. Reynolds, J.Chem.Phys., 1959, 30, 1422.
10. W. McFarlane, J.Chem.Soc.(A), 1968, 2280.
11. W. McFarlane, Chem.Comm., 1968, 393.
12. R.R. Dean, J.C. Green, J.Chem.Soc.(A), 1968, 3047.
13. N.F. Ramsey, Phys.Rev., 1950, 78, 699.
14. W. McFarlane, Chem.Comm., 1969, 700.
15. W. McFarlane, J.Chem.Soc.(A), 1967, 1922.
16. W. McFarlane, Chem.Comm., 1967, 772.
17. S.O. Grim, R.L. Keiter, W. McFarlane, Inorg.Chem., 1967, 6, 1133.

18. G. Socrates, J.Inorg.Nucl.Chem., 1969, 31, 1667.

19. A. Pidcock, R.E. Richards, L.M. Venanzi, J.Chem.Soc.(A), 1966, 1707.

20. B.T. Heaton, A. Pidcock, J.Organomet.Chem., 1968, 14, 235.

21. S.S. Zumdahl, R.S. Drago, J.Amer.Chem.Soc., 1968, 90, 6669.

22. F.H. Allen, S.N. Sze, J.Chem.Soc.(A), 1971, 2054.

23. F.H. Allen, A. Pidcock, C.R. Waterhouse, J.Chem.Soc.(A), 1970, 2087.

24. D.W.W. Anderson, J.E. Bentham, D.W.H. Rankin, J.Chem.Soc. Dalton, 1973, 1215.

25. E.A.V. Ebsworth, J.J. Turner, J.Phys.Chem., 1963, 67, 83.

26. E.A.V. Ebsworth, G.M. Sheldrick, Trans.Faraday Soc., 1966, 62, 3282.

27. D.E.J. Arnold, J.S. Dryburgh, E.A.V. Ebsworth, D.W.H. Rankin, J.Chem.Soc. Dalton, 1972, 2518.

28. P.C. Lauterbur, R.J. Kurland, J.Amer.Chem.Soc., 1962, 84, 3405.

29. J.E. Bentham, S. Cradock, E.A.V. Ebsworth, J.Chem.Soc. (A), 1971, 587.

30. J.E. Bentham, Ph.D. Thesis, Edinburgh, 1970.

31. J. Chatt, L.A. Duncanson, B.L. Shaw, Chem. and Ind., 1958, 36, 859.

32. L. Malatesta, C. Cariello, J.Chem.Soc., 1958, 2323.

33. J.A. Chapoorian, J. Lewis, R.S. Nyholm, Nature, 1961, 190, 528.

34. L. Malatesta, R. Ugo, J.Chem.Soc., 1963, 2080.

35. C.J. Nyman, C.E. Wymore, G. Wilkinson, J.Chem.Soc.(A), 1968, 561.

36. F. Glockling, K.A. Hooton, J.Chem.Soc.(A), 1968, 826.

37. F. Cariati, R. Ugo, F. Bonati, Inorg.Chem., 1966, 5, 1128.

38. J.T. Dumler, D.M. Roundhill, J. Organometallic Chem., 1971, 30, C35.

39. U. Belluco, U. Croatto, P. Uguagliah, R. Pietropaolo, Inorg.Chem., 1967, 6, 718.

40. R.J. Cross, F. Glockling, J.Chem.Soc., 1965, 5422.

41. E.H. Brooks, R.J. Cross, F. Glockling, Inorg.Chim.Acta. 1968, 2, 17.

42. R.J. Cross, Organometallic Chem.Rev., 1967, 2, 97.

43. C.D. Falle, J. Halpern, J.Amer.Chem.Soc., 1965, 87, 3523.

44. U. Belluco, M. Guistinani, M. Graziani, J.Amer.Chem.Soc. 1967, 89, 6494.

45. W. McFarlane, R.F.M. White, Chem.Comm., 1969, 439.

46. J.A. Osborn, F.H. Jardine, J.F. Young, G. Wilkinson, J.Chem.Soc.(A), 1966, 1711.

47. J.H. Nelson, H.B. Jonassen, D.M. Roundhill, Inorg.Chem., 1969, 8, 2591.

48. F. Glockling, M.D. Wilbey, J.Chem.Soc.(A), 1970, 1675.

49. J.F. Young, Adv.Inorg.Chem. and Radiochem., 1968, 11, 92.

50. F. Glockling, "The Chemistry of Germanium", Academic Press, London, 1969.

51. F.R. Hartley, "The Chemistry of Platinum and Palladium", Applied Science Publishers Ltd., London, 1973.

52. C. Eaborn, R.W. Bott in "Organometallic Compounds of 'Group IV Elements" Dekker, New York, 1968, 1 pp.213 - 273.

53. T.S. Piper, O. Lemal, G. Wilkinson, Naturwisseschaften, 1956, 43, 129.

54. R.S. Gorsich, J.Amer.Chem.Soc., 1962, 84, 2486.

55. D. Seyferth, H.P. Hofmann, R. Burton, J.F. Helling, Inorg. Chem., 1962, 1, 227.

56. B.J. Aylett, J.M. Campbell, Chem.Comm., 1965, 217.

57. B.J. Aylett, J.M. Campbell, J.Chem.Soc.(A), 1969, 1910.

58. B.J. Aylett, J.M. Campbell, J.Chem.Soc.(A), 1969, 1916.

59. E.A.V. Ebsworth, "Volatile Silicon Compounds", Pergamon, Oxford, 1963.

60. S.R. Gunn, L.G. Green, J.Phys.Chem., 1961, 65, 779.

61. A.G. Massey, A.J. Park, F.G.A. Stone, J.Amer.Chem.Soc. 1963, 85, 2021.

62. E.A.V. Ebsworth in, "Organometallic Compounds of the Group IV Elements", Dekker, New York, 1968, pp.1 - 104.

63. K.M. Mackay, R.D. George, J.Inorg.Nucl.Chem.Letters, 1969, 5, 797.

64. W. Jetz, P.R. Simmons, J.A.J. Thompson, W.A.G. Graham, Inorg.Chem., 1966, 5, 2217.

65. W. Jetz, W.A.G. Graham, J.Amer.Chem.Soc., 1967, 89, 2773.

66. W.A.G. Graham, Inorg.Chem., 1968, 7, 315.

67. A.P. Hagen, A.G. MacDiarmid, Inorg.Chem., 1967, 6, 686.

68. S. Cradock, E.A.V. Ebsworth, A. Robertson, J.Chem.Soc. Dalton, 1973, 22.

69. R.J. Cross, F. Glockling, Proc.Chem.Soc., 1964, 143.

70. R.J. Cross, F. Glockling, J.Chem.Soc., 1965, 5422.

71. J. Chatt, C. Eaborn, S.D. Ibekwe, P.N. Kapoor, J.Chem. Soc.(A), 1970, 1343.

72. F. Glockling, K.A. Hooton, Chem.Comm., 1966, 218.

73. F. Glockling, K.A. Hooton, J.Chem.Soc.(A), 1967, 1066.

74. J. Chatt, C. Eaborn, P.N. Kapoor, J.Chem.Soc.(A), 1970, 881.

75. F. Glockling, K.A. Hooton, J.Chem.Soc.(A), 1968, 826.

76. J.E. Bentham, S. Cradock, E.A.V. Ebsworth, J.Chem.Soc. (A), 1971, 587.

77. E.H. Brooks, F. Glockling, J.Chem.Soc.(A), 1966, 1241.

78. J.E. Bentham, Ph.D. Thesis, Edinburgh, 1970.

79. D.A. Harbourne, F.G.A. Stone, J.Chem.Soc.(A), 1968, 1765.

80. R.J. Cross, R. Wardle, J.Chem.Soc.(A), 1971, 2000.

81. Y. Ustynyuk, A.V. Kisin, A.A. Zenkin, J.Organomet.Chem., 1972, 37, 101.

82. R.N. Golberg, L.G. Hepler, Chem.Rev., 1968, 229.

83. C. Glidewell, personal communication.

84. J.M. Jenkins, B.L. Shaw, Proc.Chem.Soc., 1963, 279.

85. G.W. Parshall, J.Amer.Chem.Soc., 1965, 87, 2133.

86. P.L. Goggin, R.J. Goodfellow, S.R. Haddock, (in part) J.G. Eary, J.Chem.Soc.Dalton, 1972, 647.

87. J.E. Bentham, E.A.V. Ebsworth, Inorg.Nucl.Chem.Letters, 1970, 6, 671.

88. A. Davidson, P.E. Rakita, Inorg.Chem., 1970, 9, 289.

89. A.P. Hagan, P.J. Russo, J. Organomet.Chem., 1973, 51, 125.

90. S.L. Manatt, G.L. Juvinall, R.I. Wagner, D.D. Elleman, J.Amer.Chem.Soc., 1966, 88, 2689.

91. J. Chatt, B.L. Shaw, J.Chem.Soc., 1959, 705.

92. J. Chatt, B.L. Shaw, J.Chem.Soc. 1959, 4020.

93. G. Calvin, G.E. Coates, J.Chem.Soc., 1960, 2008.

94. E.H. Brooks, F. Glockling, Chem.Comm., 1965, 510.

95. B. Crociani, T. Boschi, U. Belluco, Proc.Third Int.Inorg.Chem. Acta Symposium, Venice, 1970, B.1.

96. G. Cartwan, G. Deganello, T. Boschi, U. Belluco, J.Chem. Soc.(A), 1969, 1142.

97. R.M. Izatt, D.J. Eatouch, C.E. Morgan, J.J. Christensen, J.Chem.Soc.(A), 1970, 2514.

98. H.B. Wellman, J.Amer.Chem.Soc., 1930, 52, 985.

99. E.H. Brooks, F. Glockling, J.Chem.Soc.(A), 1967, 1030.

100. H. Munakata, M.L.H. Green, Chem.Comm., 1970, 881.

101. K. Kudo, M. Hidai, T. Murayama, Y. Uchida, Chem.Comm., 1970, 1701.

102. S. Sternhell, Quarterly Rev. 1969, 23, 236.

103. M.C.L. Gerry, J.C. Thompson, T.M. Sugden, Nature, 1966, 211, 846.

104. D.R. Jenkins, R. Kewley, T.M. Sugden, Trans.Farad.Soc., 1962, 58, 1284.

105. E.A.V. Ebsworth, R. Mould, R. Taylor, G.R. Wilkinson, L. A. Woodward, Trans.Farad.Soc., 1962, 58, 1069.

106. S.J. Cyvin, J. Brunvoll, A.G. Robiette, Chem.Phys. Letters, 1971, 11, 263.

107. E.A.V. Ebsworth, D.R. Jenkins, M.J. Mays, T.M. Sugden, Proc.Chem.Soc., 1963, 21.

108. J.D. Murdoch, D.W.H. Rankin, Chem.Comm., 1972, 748.

109. K.R. Ramaprasad, R. Varma, R. Nelson, J.Amer.Chem. Soc., 1968, 90, 6247.

110. D.W.H. Rankin, S.J. Cyvin, J.Chem.Soc., Dalton, 1972, 1277.

111. S. Cradock, E.A.V. Ebsworth, J.D. Murdoch, J.Chem.Soc. Faraday II, 1972, 68, 86.

112. S. Cradock, D.W.H. Rankin, J.Chem.Soc. Faraday II, 1972, 68, 940.

113. L. Pauling, L.O. Brockway, J.Amer.Chem.Soc., 1937, 59, 13.

114. R.G. Lett, W.H. Flygare, J.Chem.Phys., 1967, 47, 4730.

115. C.I. Beard, B.P. Darley, J.Amer.Chem.Soc., 1949, 71, 929.

116. D.W.W. Anderson, D.W.H. Rankin, A. Robertson, J.Mol. Structure, 1972, 14, 385.

117. N. Muller, R.C. Bracken, J.Chem.Phys., 1966, 32, 1577.

118. J. Sheridan, A.C. Turner, Proc.Chem.Soc., 1960, 21.

119. J.S. Muenter, V.W. Laurie, J.Chem.Phys., 1963, 39, 1181.

120. M.C.L. Gerry, T.M. Sugden, Trans.Farad.Soc., 1965, 61, 2091.

121. L.F. Thomas, E.J. Sherrard, J. Sheridan, Trans.Farad. Soc., 1955, 51, 619.

122. C. Glidewell, personal communication.

123. G.C. Holywell, D.W.H. Rankin, B. Beagley, J.M. Freeman, J.Chem.Soc.(A), 1971, 785.

124. S.J. Cyvin, "Molecular Vibrations and Mean Square Amplitudes", Universitetsforlaget, Oslo, Elsevier, Amsterdam, 1968.

125. D. M. Bridges, G.C. Holywell, D.W.H. Rankin, J.M. Freeman, J.Organomet.Chem., 1971, 32, 87.

126. C. Glidewell, A.G. Robiette, G.M. Sheldrick, personal communication.

127. R. Varma, K.S. Buckton, J.Chem.Phys., 1967, 46, 1565.

128. E.C. Thomas, V.W. Laurie, J.Chem.Phys., 1964, 44, 2602.

129. J. Dale in "Chemistry of Acetylenes", Dekker, New York, 1969, pp.4.

130. J.N. Shoolery, R.G. Shulman, W.F. Sheehan, V. Schomaker, D.M. Yost, J.Chem.Phys., 1951, 19, 1364.

131. H.C. Clark, W.S. Tsang, J.Amer.Chem.Soc., 1967, 89, 529.

132. C. Eaborn, A. Pidcock, B. Ratcliff, J. Organomet.Chem., 1972, 43, C5.

133. D. Morelli, A. Segre, R. Ugo, G. La Monica, S. Cenini, F. Conti, B. Bonati, Chem.Comm., 1967, 524.

134. A. Charles, W. McFarlane, Molec.Phys., 1968, 14, 299.

135. B. Beagley, A.H. Clark, T.G. Hewitt, J.Chem.Soc.(A), 1968, 658.

136. K. Hedberg, M. Iwasaki, Acta.Chryst., 1964, 17, 529.

137. H.L. Cox, R.A. Bonham, J.Chem.Phys., 1967, 47, 2599.

138. L.S. Bartell, J.Chem.Phys., 1955, 23, 1219.

139. A.E. Finholt, A.C. Bond, K.E. Wilzbach, H.L. Schlesinger, J.Amer.Chem.Soc., 1947, 2692.

140. G. Fritz, D. Kumner, Z.Anorg.Chem., 1961, 308, 105.

141. G.M. Sheldrick, Ph.D. Thesis, Cambridge, 1966.

142. J.C. Thompson, Ph.D. Thesis, Cambridge, 1965.

143. A.R. Conrad, Ph.D. Thesis, Cambridge, 1967.

144. W.L. Jolly, J.Amer.Chem.Soc., 1961, 83, 335.

145. L.M. Dennis, P.R. Judy, J.Amer.Chem.Soc., 1929, 51, 2321.

146. W.G. Finnegan, W.P. Norris, J.Organ, Chem., 1963, 1139.

147. O. Dimrorh, W. Wislicenus, Ber.Deut.Chem.Ges., 1905, 38, 1573.

148. R.A. Jensen, Z. Anorg.Chem., 1936, 229, 225.

149. P.L. Goggin, R.J. Goodfellow, J. Chem.Soc.(A), 1966, 1462.

150. J. Chatt, B.L. Shaw, J.Chem.Soc., 1962, 5075.

151. A. Peloso, G. Dolcatti, J.Chem.Soc.(A), 1967, 1944.

152. M.I. Bruce, D.A. Harbourne, F. Waugh, F.G.A. Stone, J.Chem.Soc.(A), 1968, 356.

153. F.G. Mann, D. Purdie, J.Chem.Soc., 1935, 1549.